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# Evidence for the Kondo effect in Zn:Fe films: A $^{57}$Fe Mössbauer effect study

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Zn films doped with $^{57}$Fe (atomic concentration $c$ between 0.2 and 2.0 at. %) have been prepared by the coevaporation of the two metals onto a cooled substrate ($T_s$=80 K). *In situ* electrical resistance measurements on these films show resistance minima at $T_K$ ($T_K$=10 K for $c$=1.0 at. %) which disappear in an external magnetic field $B_{\mathrm{ex}}$=5 T and, therefore, are interpreted as Kondo minima. $^{57}$Fe Mössbauer effect studies on the films with $c$=0.6 at. % taken at $T$=4.3 K and for various $B_{\mathrm{ex}}$ values reveal that the effective paramagnetic Fe moments $\mu$ are $\mu<0.1\mu_B$ for $B_{\mathrm{ex}}$=3 T. For larger magnetic fields the magnitude of $\mu$ is increasing with increasing $B_{\mathrm{ex}}$ [$\mu\sim 0.30(3)\mu_B$ for $B_{\mathrm{ex}}$=7 T], as expected for a spin-compensated Kondo state.

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## I. INTRODUCTION

Local magnetic moments of 3*d* atoms in *sp* metals usually are quenched due to the formation of a spin-compensated Kondo state. This has been experimentally proven, for example, for Fe impurity atoms in Zn: using heavy-ion recoil implantation, combined with the online time-differential angular distribution (TDPAD) method, Riegel *et al.* have shown that $^{54}$Fe impurities in Zn are nonmagnetic with high accuracy, i.e., that the local magnetic susceptibility $\beta-1$ of the $^{54}$Fe ions in an external magnetic field of 2 T is $\beta-1 \leqslant 0.01$.[1]

Due to advances in sample preparation methods nowadays it is possible to investigate the behavior of impurities in metals throughout the periodic table without the need of using methods that involve heavy-ion accelerators, like heavy-ion recoil implantation. It has been shown, for example, that it is possible to prepare samples of Zn or Cd hosts, which contain $^{57}$Fe impurities at a concentration of the order of 1 at. %, by using the vapor-quenching method.[2] Such samples have been investigated in the past by standard $^{57}$Fe Mössbauer effect (ME) spectroscopy.[2] The main interest of these former studies was to get information on the isomer shift (IS) of $^{57}$Fe atoms on substitutional lattice sites in the hcp Zn lattice and to compare these results with those of theoretical *ab initio* calculations.[3] We now have extended these experiments to (i) *in situ* resistance measurements and (ii) $^{57}$Fe ME studies in an external magnetic field. While the experiments (i) may give us information about the possible existence of a Kondo state via the finding of a resistance minimum, the studies (ii) will give information on the local magnetic moment $\mu_B$ of Fe in Zn and the possible change of $\mu_B$ with $B_{\mathrm{ex}}$. Similar $^{57}$Fe ME experiments were performed a long time ago to study the Kondo effect of Fe impurities in noble metals and certain *d*-band metal hosts.[4] We do not know of any such studies with $^{57}$Fe impurities in a Zn host. In addition it should be mentioned that our studies are performed at relatively high Fe atomic concentrations, far beyond the usually accepted limit for pure Kondo systems.

## II. EXPERIMENTAL PROCEDURE

Films of Zn doped with $^{57}$Fe between 0.2 and 2.0 at. % were prepared in a variable-temperature $^4$He cryostat by thermal coevaporation of high-purity Fe (98% enriched $^{57}$Fe) and Zn (99.999%) metals from two independent resistively heated Ta ovens. The deposition was performed onto kapton substrates tilted 45° relative to the vapor metal flux direction and the $\gamma$-ray direction in the $^{57}$Fe Mössbauer effect studies. Four Ag electrodes have been evaporated on the kapton substrate before film deposition in order to perform *in situ* resistance measurements on the as-prepared films using the four-probe ac method. The substrate temperature $T_s$ during sample deposition was 80 K. Such a low deposition temperature has to be taken in order to prevent Fe-cluster formation due to surface migration during deposition of Zn and Fe atoms, respectively. Lower temperatures during sample deposition were not possible in our $^4$He cryostat at the time of the experiment. The residual pressure in the deposition chamber during sample deposition was about $2\times10^{-8}$ mbar. The deposition rates were controlled by quartz crystals. Deposition rates for Zn were about 0.2 nm/s. All films had a nominal thickness of about 400 nm. Our experimental setup[5] is especially suitable for *in situ* $^{57}$Fe ME studies of the as-prepared as well as annealed films. Additional $^{57}$Fe ME experiments have been performed *ex situ* in a variable-temperature $^4$He cryostat with a built-in superconducting magnet ($B_{\mathrm{ex}}\leqslant 7$ T). The ME experiments were performed using a 25 mCi $^{57}$Co:Rh source moving in a sinusoidal mode.

## III. RESULTS AND DISCUSSION

### A. Resistance measurements

We have plotted in Fig. 1 the *in situ* measured resistance $R$ of five Zn:Fe samples with Fe atomic concentration of $c$=0, 0.2, 0.6, 1.0, and 1.5 at. %, respectively, as a function of temperature $T$, the latter on a logarithmic scale. One clearly sees resistance minima and a logarithmic increase of $R$ on decreasing $T$ below the minima. Both facts, the resistance minimum and the logarithmic increase in $R$, are typical for Kondo systems. In the inset of Fig. 1 we show the same plot of $R(T)$ for the sample with the highest Fe atomic concentration of $c$=2.0 at. %. One clearly can see that $R(T)$ of this sample does not show a logarithmic increase of $R$

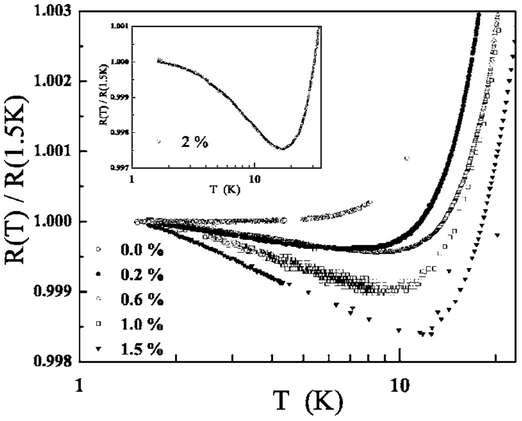

FIG. 1. Resistance of Zn:Fe samples with different Fe atomic concentrations as given in the figure. Note the logarithmic scale of the temperature $T$. The inset gives the resistance of the sample with 2 at. % Fe, also with a logarithmic scale of $T$.

with decreasing $T$ below the resistance minimum. This is an indication that at such a high Fe atomic concentration the Kondo behavior is strongly disturbed. In Fig. 2 we have plotted the temperature $T_K$ of the resistance minima for all samples as a function of Fe atomic concentration $c$. The dashed line is a fit assuming that $T_K \propto c^{1/5}$, as expected for the change of the Kondo temperature with magnetic impurity concentration $c$.[6] Again we can see that all samples with $c \leqslant 1$ at. % have a $T_K$ which is in agreement with the expected Kondo behavior while the sample with $c=2$ at. % definitely deviates from such a behavior. A further confirmation of Kondo behavior can be obtained from resistance measurements in an external magnetic field $B_{\mathrm{ex}}$. We show in Fig. 3 the resistance of the sample with $c=1.0$ at. % for $B_{\mathrm{ex}}=5$ T compared to the resistance for $B_{\mathrm{ex}}=0$. One clearly sees the disappearance of the minimum for $B_{\mathrm{ex}}=5$ T, typical for Kondo systems where the Kondo state is destroyed in large enough external magnetic fields (see also the Sec. III B). Finally we want to mention that resistance minima that disappear in magnetic fields can also be caused by the so-called weak localization, typical for highly disordered systems. The x-ray diffraction (XRD) pattern of our film show quite narrow difraction lines [see the XRD pattern of the sample with $c=0.6(2)$ at. % Fe in Fig. 5] which indicates that there is no strong disorder in our sample.

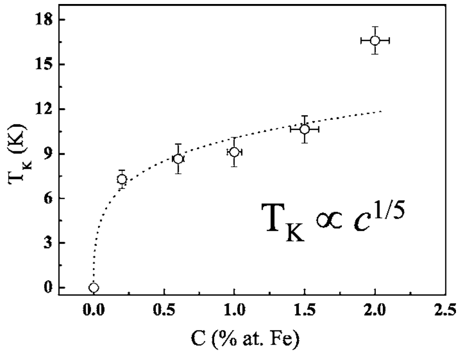

FIG. 2. Temperature $T_K$ of the resistance minima as a function of Fe atomic concentration $c$. The dashed curve gives the behavior $T_K(c)$ as expected for Kondo systems (Ref. 6).

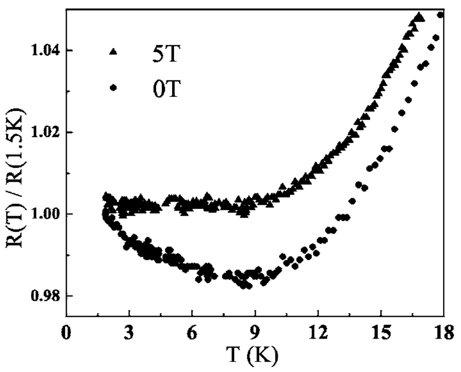

FIG. 3. Resistance of Zn:Fe sample with $c=1$ at. % Fe without and with applied external field of $B_{\mathrm{ex}}=5$ T.

However, we cannot completely rule out weak localization as being responsible for the observed resistance behavior. For that reason we have performed additional experiments (see below), where we have used a local method, namely, $^{57}$Fe Mössbauer spectroscopy, in order to study the local $^{57}$Fe moments.

### B. Mössbauer studies

The $^{57}$Fe ME spectrum of the film with an Fe atomic concentration $c=0.6(2)$ at. %, prepared at $T_s=80$ K, has been measured *in situ* at 300 K. It exhibits an asymmetric quadrupole doublet as shown in Fig. 4(a). A similar asymmetry already has been observed in the previous reported spectra in films having about the same Fe concentration but prepared at $T_s=300$ K. This asymmetry has been interpreted as caused by a texture in our deposited Zn film.[2] In order to confirm that such an interpretation is also correct for the film that we have now prepared at $T_s=80$ K, we have removed the film from the cryostat and measured the $^{57}$Fe ME spectrum *ex situ* in another $^4$He cryostat with a different geometry: while the direction of the $\gamma$ rays relative to the film plane had an angle of $\alpha=45°$ in the *in situ* experiment, the angle in the *ex situ* measurement was $\alpha=90°$ [see insets in Figs. 4(a) and 4(b)]. The *ex situ* $^{57}$Fe ME spectrum obtained

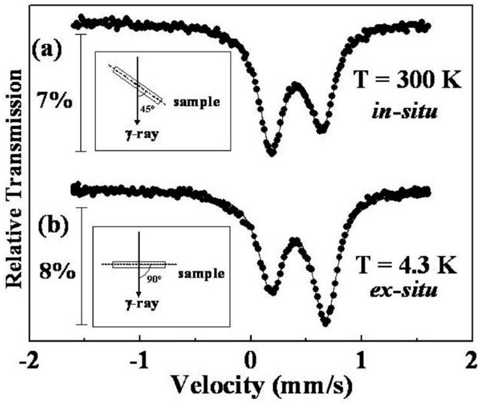

FIG. 4. $^{57}$Fe ME spectra of sample with $c=0.6$ at. % Fe measured at different geometries as given in the insets of this figure.

TABLE I. Values of hf parameters of $^{57}$Fe ME spectra shown in Fig. 4.

| | | | | $\alpha$ (°) | |
|---|---|---|---|---|---|
| $T$ (K) | IS (mm/s) | $\Delta E_Q$ (mm/s) | $W$ (mm/s) | $V_{zz}<0$ | $V_{zz}>0$ |
| 300 | 0.52(1) | 0.45(2) | 0.28(1) | 46(2) | 58(2) |
| 4.3 | 0.54(1) | 0.48(2) | 0.27(1) | 88(2) | 39(2) |

at 4.3 K is displayed in Fig. 4(b), which clearly shows that the asymmetry in the quadrupolar split spectrum has changed its sign. The spectra in Figs. 4(a) and 4(b) have been fitted with one single quadrupole doublet assuming an angle $\alpha$ between the main component of the electric field gradient tensor $V_{zz}$ and the $\gamma$-ray direction. The results of these fittings are given in Table I. While all hyperfine (hf) parameters essentially are the same for both spectra [the small changes in the isomer shift (IS) and the quadrupole splitting ($\Delta E_Q$) values due to the temperature difference between the two measurements are irrelevant in this context], the value of $\alpha$ going from the *in situ* to the *ex situ* geometry changes from 46(2)° to 88(2)° if we assume $V_{zz}<0$ and from 58(2)° to 39(2)° if we assume $V_{zz}>0$. The values of $\alpha$ for $V_{zz}<0$ are within the experimental errors identical with those of the angle between the $\gamma$-ray direction and the film plane. We can conclude that $V_{zz}<0$ and is lying in the film plane. This conclusion on the sign of $V_{zz}$ is independently confirmed by the $^{57}$Fe ME experiments with external magnetic field (see below). These experiments (see spectra in Fig. 6) clearly give $V_{zz}<0$. Since the $V_{zz}$ direction for the hcp structure is given by the $c$ direction, it follows that the $c$ direction of the textured Zn films is lying in the film plane. This has been confirmed by additional x-ray diffraction measurements on our Zn films. The result of this XRD experiment is shown in Fig. 5 together with the XRD data of a solid Zn polycrystalline sample.

The dominance of the [110] diffraction peak is clear evidence for a strongly textured film with its (110) planes being parallel to the film surface. Since the $c$ direction is contained in the (110) plane, these XRD data are in perfect agreement with our ME results. The IS value of the quadrupole doublet at 300 K is 0.52(1) mm/s relative to $\alpha$-Fe at room temperature and the quadrupole splitting is 0.45(2) mm/s. Both hf parameters are the same as those reported for the 0.5 at. % doped Zn film prepared at 300 K.[2] For that reason we give the same interpretation of this doublet: it is assigned to Fe atoms on substitutional lattice sites in the hcp Zn lattice. This assignment mainly is based on comparison of the measured IS value with that obtained from theoretical calculations.[3] The Mössbauer spectra do not indicate the presence of any other Fe component, e.g., Fe dimers or even larger Fe clusters, in our sample.

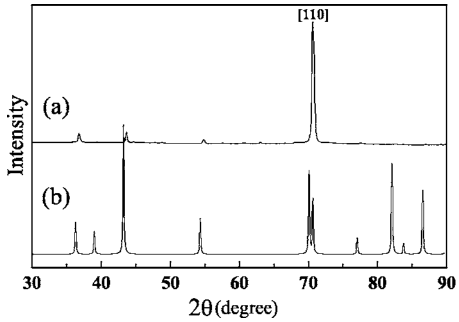

FIG. 5. (a) X-ray diffraction of Zn film containing 0.6 at. % Fe, deposited at 80 K. (b) XRD of Zn polycrystalline sample.

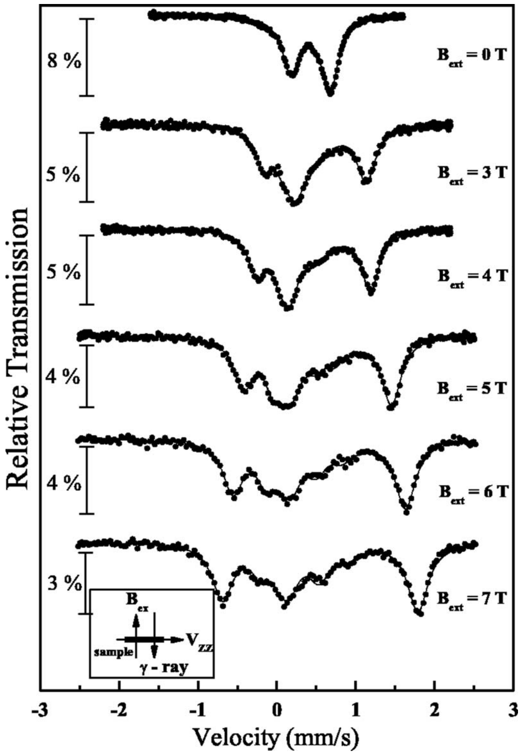

FIG. 6. $^{57}$Fe ME spectra of sample with $c=0.6$ at. % Fe measured at 4.3 K in external magnetic fields $B_{\mathrm{ex}}$ parallel to the $\gamma$-ray direction and perpendicular to the sample surface (see inset of this figure). $B_{\mathrm{ex}}$ values are given in the figure.

In order to see if the Fe atoms in our Zn film carry any magnetic moment it is not enough just to lower the temperature down to 4.3 K in the case that the sample is paramagnetic, which is what we would expect since our sample has an Fe atomic concentration far below the magnetic percolation limit. The $^{57}$Fe ME spectrum taken at this temperature [see Fig. 4(b)] clearly shows a nonmagnetic quadrupole doublet, which might be due to either a vanishing Fe magnetic moment or fast paramagnetic spin relaxation. In order to find out what is the true treason, an external magnetic field has to be applied, which will suppress fast paramagnetic relaxation.

Figure 6 shows the $^{57}$Fe ME spectra taken at T=4.3 K in external magnetic fields $B_{\mathrm{ex}}$, with the following geometry (see also inset in Fig. 6): $B_{\mathrm{ex}}$ perpendicular to the film plane (or $V_{zz}$) and parallel to the $\gamma$-ray direction. These spectra have been fitted with one free fitting parameter only, namely, the value of the effective magnetic hf field $B_{\mathrm{eff}}=B_{\mathrm{ex}}-B_{\mathrm{hf}}$, where $B_{\mathrm{hf}}$ is the magnetic hf field at the $^{57}$Fe nucleus without external magnetic field. All other parameters either already have been obtained from the spectrum in Fig. 4(b) (see also Table I) or are given by the geometry (the angle between $V_{zz}$

TABLE II. Values of effective magnetic hf field $B_{ex}$ and of magnetic hf field $B_{hf}$, as obtained from fittings to the $^{57}$Fe ME spectra shown in Fig. 6.

| $B_{ex}$ (T) | $B_{eff}$ (T) | $B_{hf}$ (T) |
|---|---|---|
| 0 | 0 | 0 |
| 3 | 3.0(2) | 0.0(2) |
| 4 | 3.4(2) | 0.6(2) |
| 5 | 4.4(2) | 0.6(2) |
| 6 | 5.3(2) | 0.7(2) |
| 7 | 6.1(2) | 0.9(2) |

and $B_{ex}$ and the angle between $V_{zz}$ and $\gamma$-ray direction are both 90°). As one can see from Fig. 6 the agreement between the measured spectra and the fit is excellent, which again confirms our interpretation of the asymmetric quadrupole doublet as being due to a highly textured Zn film with $V_{zz}$ lying in the film plane. The $B_{eff}$ values obtained for the different values of $B_{ex}$ are given in Table II. For $B_{ex} < 3$ T the value of $B_{eff}$ is within the experimental errors the same as that of $B_{ex}$, i.e., $B_{hf}=0$. For larger $B_{ex}$ values $B_{eff}$ is slightly smaller than $B_{ex}$, having the largest difference $B_{ex}-B_{eff} = B_{hf}=0.9(2)$ T for $B_{ex}=7$ T. We now can estimate the saturation magnetic hf field $B_{hf}(0)$ from the measured hf field $B_{hf}$ at 4.3 K using the relation $B_{hf}=B_{hf}(0)\ B_J[\mu(0)B_{ex}/k_BT]$ which is valid in the ideal paramagnetic case. $B_J$ is the Brilluoin function for angular momentum $J$, and $\mu(0)$ is the effective saturation magnetic moment of Fe, which can be related to $B_{hf}(0)$ using the common approximation for metallic systems: $B_{hf}(0)/\mu=15$ T. We further assume $J=2$ (high-spin Fe$^{2+}$) which, however, is not an essential point. An estimated upper limit for the effective magnetic moment in zero external magnetic field can be obtained from the experimental fact that no magnetic hf field is observed at $B_{ex}<3$ T: $\mu(0) < 0.1\mu_B$ or $B_{hf}(0) < 1.5$ T at $B_{ex}<3$ T. On the other hand, a value of $\mu(0)=0.30(3)\mu_B$ for the effective saturation magnetic moment, corresponding to a saturation magnetic hf field of $B_{hf}(0)=4.5(5)$ T, is obtained for an external magnetic field of 7 T.

In the following we want to discuss our results in comparison with those found (i) by Riegel *et al.*[1] in their TDPAD studies of heavy-ion-recoil-implanted $^{54}$Fe in Zn and (ii) by $^{57}$Fe ME studies in other Kondo systems, e.g., Cu:Fe (Ref. 7) or Ag:Fe.[8] (i) The TDPAD studies, which have been performed in an external magnetic field of 2 T, did not show any local magnetic susceptibility at the $^{54}$Fe site. This is in perfect agreement with our $^{57}$Fe result, which does not show any local hf field at the $^{57}$Fe site in external magnetic fields below 3 T. Thus, both methods, ion implantation at 300 K and vapor quenching at 80 K, result in Fe-doped Zn samples which show that there is no magnetic moment at the Fe site, i.e., indicate that it is a Kondo system. However, there is an essential difference between the two samples: our $^{57}$Fe concentration of 0.6 at. % is orders of magnitude larger than that in the TDPAD studies. It is quite astonishing that one still has a Kondo system at an Fe atomic concentration which is about two orders of magnitude larger than the usually accepted Kondo limit lying in the 100 ppm region. (ii) $^{57}$Fe ME studies on the Kondo systems Cu:Fe and Ag:Fe reveal that the external magnetic fields necessary to destroy the Kondo state at temperatures far below the Kondo temperature $T_K$ are 20 T (Ref. 7) for Cu:Fe having $T_K=26$ K and about 3 T (Ref. 8) for Ag:Fe having $T_K=1.8$ K. Our finding, that in the Zn:Fe sample with $T_K=8$ K an external field of 7 T strongly disturbs the Kondo state at 4.3 K, therefore, seems quite reasonable. Even the obtained saturation magnetic hf fields (8.5 and 3.6 T for Cu:Fe and Ag:Fe, respectively) are comparable with the value of 4.5(5) T we have found for Zn:Fe.

## IV. CONCLUSIONS AND OUTLOOK

Resistance as well as $^{57}$Fe ME experiments clearly indicate that the system Zn:Fe behaves like a Kondo system for Fe atomic concentrations up to 1.5 at. %. Such high impurity concentrations are far beyond the limit usually accepted for a pure Kondo state. For the moment we do not know why the Kondo state survives up to such high concentrations in the Zn:Fe system. However, we found clear evidence that the Kondo behavior is strongly disturbed for slightly higher Fe concentrations, namely, $c=2$ at. %. Systematic $^{57}$ME experiments as a function of temperature and external magnetic field in this concentration region should be performed in order to understand the crossover between a Kondo state and a finally ordered magnetic state.

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