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MOSSBAUER EFFECT MEASUREMENTS ON MAGNETIC IMPURITIES IN METALS

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ABSTRACT

Recent Mössbauer experiments on magnetic impurities in nonmagnetic metal hosts are presented. For *Yb:Au* and *Er:Au* relaxation effects and effects from excited crystal field states are observed in the Mössbauer spectra. For *Fe:Cu* and *Fe:Au* the local magnetization as measured by the Mössbauer technique shows the typical behavior of a Kondo system. In addition for *Fe:Au* at low temperatures impurity-impurity interactions seem to play the dominant role. In $Eu_x:La_{1-x}$ magnetic order in the superconducting state has been observed in the Mössbauer spectra.

INTRODUCTION

Mössbauer experiments can measure via the hyperfine interaction the behavior of local moments in metals. They can therefore be regarded as a local probe for the microscopic properties of the moments similar to resonance methods like *ESR* or *NMR* and to other radioactive methods like *NO* or *PAC*, when compared to bulk measurements like the magnetic susceptibility, which only give spatial averages of the local moment behavior. Similar to *ESR* the advantage of the radioactive methods in this content is, that one can work in several cases in the very dilute limit of an impurity concentration of a few *ppm*, where interaction effects between impurities may not be important.

In a recent review article Narath [1] has discussed the various problems connected with hyperfine field studies of local moments in metals. In this paper I will concentrate on a few recent experiments partly performed in our laboratory, which may show the problems inherent in the Mössbauer experiments and may demonstrate the kind of understanding, Mössbauer experiments can contribute to this field. I will discuss cases, where local moments seem to be very well formed. First I discuss the so-called long relaxation limit with very long electronic relaxation times. In the experiments on *Yb:Au* [2] and on *Er:Au* [3] electronic relaxation rates could be obtained from the spectra. For *Yb:Au* [2] the influence of the Kondo effect on the electronic relaxation rate has been observed for the first time.

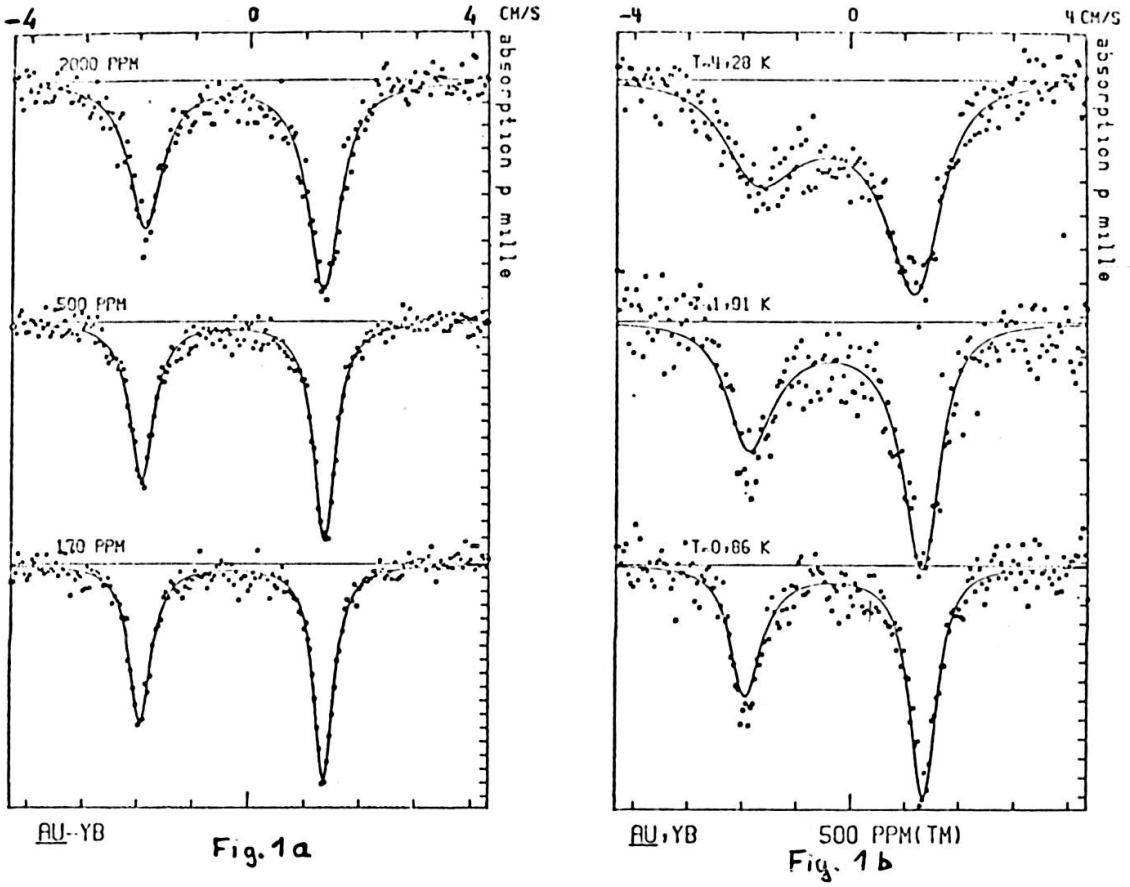
LONG RELAXATION LIMIT ($\omega_n \cdot \tau_e \gg 1$): $^{170}Yb:Au$ AND $^{166}Er:Au$

The interaction of the nuclear moment with the local electronic moment is given by the hyperfine interaction, which in the simplest case may be written as

$$H_{hf} = A \cdot \vec{I} \cdot \vec{S}$$

where I is the nuclear spin, S the spin or the effective spin of the electronic moment, and A the hyperfine coupling constant. An orbital contribution will be neglected at this time. I will come to this at a later point. In the case, that the electronic relaxation time τ_e is long compared to the nuclear Lamor periods ω_n^{-1} ($\omega_n \cdot \tau_e \gg 1$), which may be the case at low temperatures, the energy states of the coupled spin system $\vec{F} = \vec{I} + \vec{S}$ are seen in a split Mössbauer spectrum in zero external field with a line width given only by the decay time of the nuclear state. At higher temperatures the condition $\omega_n \cdot \tau_e \gg 1$ will be more or less violated due to transitions in the electronic spin system by relaxation effects. Due to this the splitting in the Mössbauer spectrum is first smeared out and finally the spectrum collapses to a single line at short relaxation times τ_e. From a careful line shape analysis one obtains the electronic relaxation rate. Relaxation effects of this kind were first observed and analysed in the system $Er:Zr$ by Hirst *et al.* [7].

Recently Gonzalez Jimenez and Imbert [2] published experiments on $Yb:Au$ using the Mössbauer effect in ^{170}Yb with the $2^+ - 0^+$ ($I_e = 2$, $I_g = 0$) 84 keV γ-transition. They used various sources of $^{170}Tm:Au$ with Tm concentrations of less than 0.2% and a single line absorber. The electronic ground state of $Yb:Au$ is a Γ_7 doublet with higher excited states at about 80 K, so that at low temperatures the electronic ground state can be described by an effective spin $S = 1/2$. In the coupled spin system $\vec{F} = \vec{I} + \vec{S}$ we get two eigenvalues ($F = 5/2$ and $F = 3/2$) for the excited nuclear state ($I_e = 2$) and one ($F = 1/2$) for the nuclear ground state ($I_g = 0$), resulting in a Mössbauer spectrum with only two lines with an intensity ratio of 2/3 in quite contrast to the well-known 5-line pattern of a $2^+ - 0^+$ transition in magnetically ordered compounds. This is seen in the low temperature Mössbauer spectra of Figure 1a at $T = 0.35\,K$. At higher temperatures (Fig. 1b) the splitting is smeared out due to an enhanced electronic relaxation rate. The relaxation rate as obtained by a detailed analysis of the spectra is shown in Figure 1c. From *ESR* experiments [8] the exchange interaction between the local moment and the conduction electrons is known to be negative. Therefore at low temperatures a deviation of the relaxation rate from the Korringa law $W/T = \text{const}$ is expected due to an enhanced scattering of the conduction electrons by the Kondo effect [9]. The logarithmic temperature dependence of W/T is clearly seen in Figure 1c in agreement with predictions by perturbation theories [9]. Within this model, a negative exchange interaction $I_{sf} = -0.55\,eV$ is obtained, which must be compared to the value



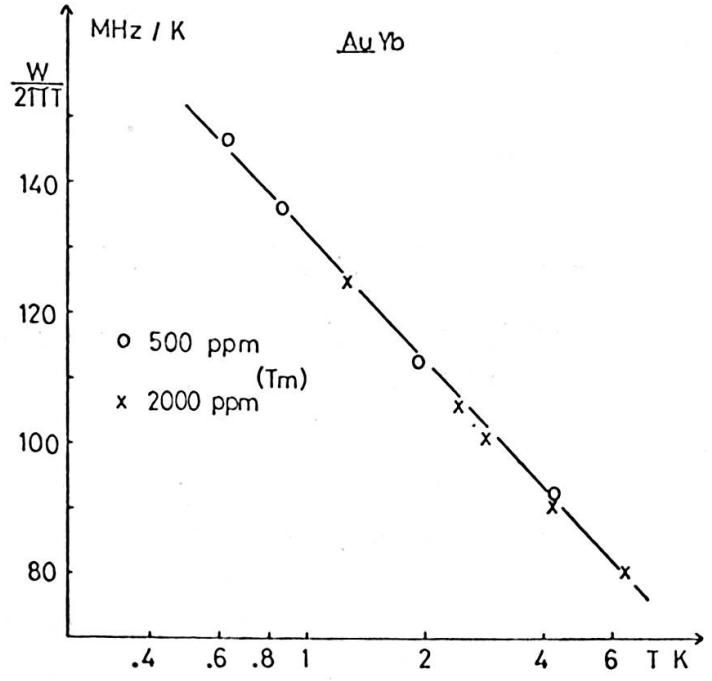


FIG. 1. — Mössbauer experiments on ^{170}Ab in *Yb : Au* from ref. 2.

a) Mössbauer spectra for various concentrations of *Tm* in *Au* at $T = 0.35$ *K*.

b) Mössbauer spectra for 500 *ppm Tm* in *Au* at various temperatures.

c) Local moment relaxation rate W/T deduced from the Mössbauer data as function of temperature.

$J_{sf} = -0.85\,(20)$ obtained from *ESR* data [8]. It must be noted, that this behavior has not been seen unequivocally in *ESR* experiments. Nuclear orientation experiments [10] indicate a very low Kondo temperature ($T_k < 10\,mK$) for *Yb:Au*. Therefore the Kondo anomalies are destroyed in very small external fields. This could be the reason, that these effects are not observed in *ESR* experiments.

Shenoy *et al.* [3] performed Mössbauer experiments on *Er:Au* using the $2^+ - 0^+$ γ-transition of ^{166}Er with sources of less than 650 *ppm Ho* in *Au* and again a single line absorber. *Er:Au* has again a Γ_7 ground state doublet with an excited Γ_8 quartet and Γ_6 doublet at 19 and 23 *K*, respectively. The 2-line spectrum of the Γ_7 ground state is clearly seen in the low temperature Mössbauer spectrum of Figure 2a. The enhanced intensity near zero velocity is attributed to impurity interactions due to clustering. This contribution is expected to be nearly temperature independent. The enhanced central intensity at higher temperatures is due to an enhanced population of the excited quartet, which gives a Mössbauer spectrum with 7 lines, totally different from the ground state spectrum. A careful analysis of the spectra including the excited crystal field states could therefore give precise values for relaxation rates and crystal field splitting. The relaxation of the ground state doublet obtained so far from the data is shown in Figure 2b. The ferromagnetic exchange interaction in this case is quite small ($I_{sf} = 0.10\,eV$ [8]). So deviations from the Korringa law at low temperatures are not expected. At higher temperatures relaxation involving higher crystal field states must be included, which would result in an enhanced relaxation for temperatures greater than 6 *K*, as observed in *ESR* experiments [11]. This seems to be absent in the Mössbauer data of Figure 2a, but this could be due to neglecting in the analysis of the spectra the direct contribution of the Γ_8 state to the Mössbauer spectrum.

FAST RELAXATION LIMIT ($\omega_n \cdot \tau_e \ll 1$): *Fe:Cu* AND *Fe:Au*

The other extreme case of fast electronic relaxation ($\omega_n \cdot \tau \ll 1$) is very easy to handle with [12]. The hyperfine interaction may then be written as

$$H_{hf} = A \cdot I_z \cdot \langle S_z \rangle$$

where $\langle S_z \rangle$ is the thermal average of the local magnetization This is a well-known normal Zeeman interaction with an effective hyperfine field $H_{hf} \alpha \langle S_z \rangle$. In this way the splitting in the Mössbauer spectrum directly reveals the behavior of the local moment as function of temperature and external field. In the absence of an interaction between the impurities $\langle S_z \rangle$ will vanish in zero external field resulting in an unsplit Mössbauer spectrum. By including interactions between impurities below an ordering temperature T_M magnetic ordering may occur with a nonvanishing average $\langle S_z \rangle$ for a given site, giving a magnetically split Mössbauer spectrum even in the absence of an external field. In this case the zero field local moment

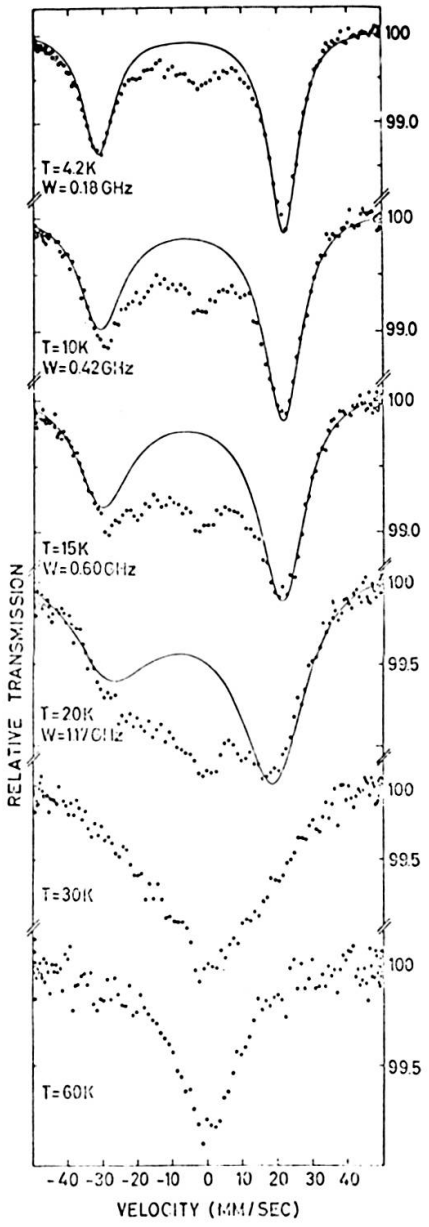


Fig. 2 a

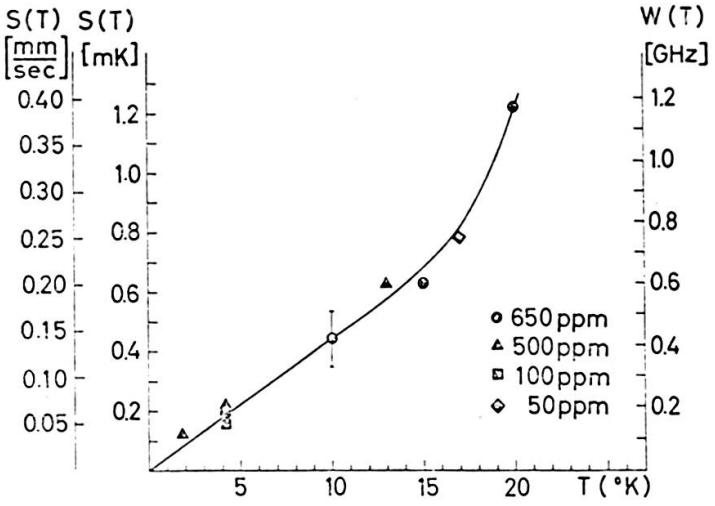


Fig. 2 b

FIG. 2. — Mössbauer experiments on ^{166}Er in *Er :Au* from ref. 3.

a) Mössbauer spectra at various temperatures.

b) Local moment relaxation rate as function of temperature.

behavior, especially its temperature dependence can be seen from Mössbauer experiments. If the electronic relaxation gets longer, the different hyperfine transitions in the Mössbauer spectrum will broaden, with the largest broadening occuring for the most split lines.

In the following I show two examples, namely *Fe :Cu* [4] and *Fe :Au* [5], on which we have performed experiments in our laboratory recently.

The Mössbauer experiments on *Fe :Cu* of Frankel *et al.* [13] showed for the first time, that at temperatures below the Kondo temperature the local moment

decreases with decreasing external field. For this system careful bulk magnetization measurements of Hurd [14] and Tholence and Tournier [15] gave the single impurity contribution to the total susceptibility. A comparison with the local susceptibility as e.g. obtained from Mössbauer experiments can show the contribution of the spatially extended conduction electrons to the local moment. An analysis of this kind was first given by Heeger [16] for this system.

We extended the Mössbauer experiments to temperatures of about $30\,mK$ in external fields up to $60\,kG$. The source was ^{57}Co diffused into a copper foil with a concentration of magnetic impurities of less than $10\,ppm$. The temperature of the source could been varied down to $30\,mK$ using a He^3/He^4-dilution refrigerator. The diamagnetic single line absorber $K_4\,^{57}Fe\,(CN)_6 \cdot H_2O$ was at a constant temperature of $1.3\,K$. Both source and absorber experienced the same external field of a superconducting magnet up to $60\,kG$ parallel to the γ-beam. Some of the Mössbauer spectra are shown in Figure 3a. All the spectra could be fitted within the fast relaxation model without linebroadening due to relaxation effects. The zero external field spectra showed an unsplit line with a temperature independent width.

To extract the local spin polarisation from the hyperfine fields one must be sure, that no orbital contribution is present [1], which is assumed to be temperature independent. By comparing the high temperature local susceptibility, as measured by the hyperfine field, with the bulk susceptibility one can extract the orbital contribution. The total susceptibility follows a Curie Weiss law with a $\theta = 30\,K$ down to the lowest temperatures. As seen from Figure 3b the local susceptibility goes linearly to zero with the total susceptibility at high temperatures. This indicates that an orbital contribution to the hyperfine field can be neglected. Taking from the high temperature data the proportionality of $-\,40\,(1)\,kG/\mu_B$ between hyperfine field and local magnetization we see (Fig. 3c), that at low temperatures the local susceptibility is larger than the total susceptibility and χ_{local}^{-1} shows a T^2 behavior at the lowest temperatures, as predicted by recent theories [17]. The deviation of the local magnetization from the total magnetization is clearly seen in Figure 3d. At low temperatures and low fields there is an antiferromagnetic contribution of a polarized conduction electron cloud to the total magnetization. This goes to zero at about $30\,K$ or $100\,kG$, values which are about equal in terms of energy and may therefore stand as a typical energy for the destruction of the Kondo state.

In order to work with a system with a smaller Kondo temperature, so that fields of $60\,kG$ are large enough to destroy the ground state correlations, we started experiments on the system *Fe :Au* [5]. For this system high temperature magnetization data of Hurd [14] give a Curie-Weiss law with $\theta_1 = 10\,K$ and $\mu_{eff} = 3.75\,\mu_B$, while low temperature experiments of two different groups [18, 19] give only $\theta_2 = 0.45\,K$ with a smaller moment $\mu_{eff} = 3.2\,\mu_B$. Both groups give arguments, that their values are due to single impurity effects. The experimental arrangements for the Mössbauer experiments were similar to the one described before in the case

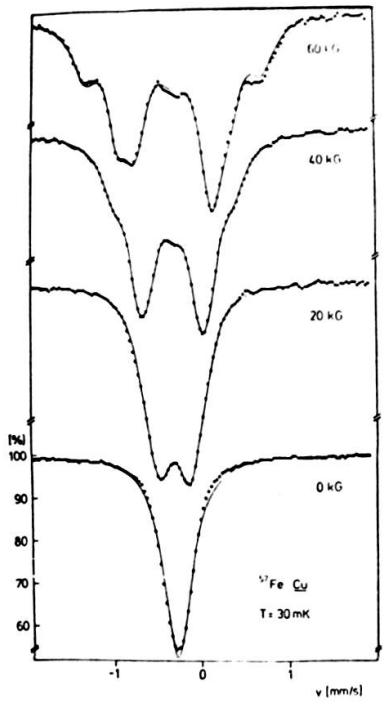


Fig. 3 a

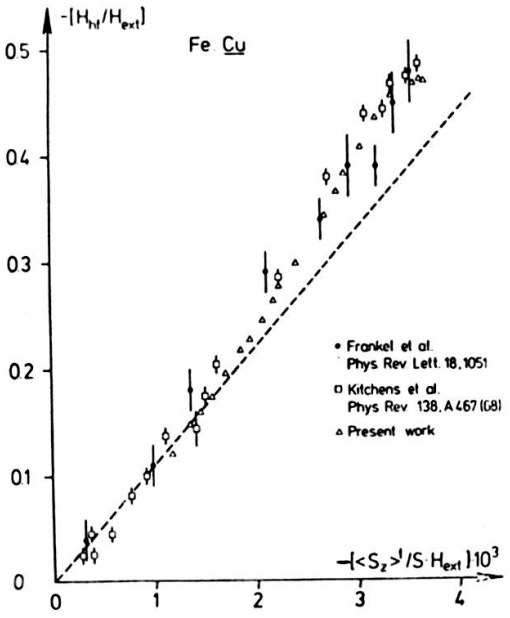


Fig. 3 b

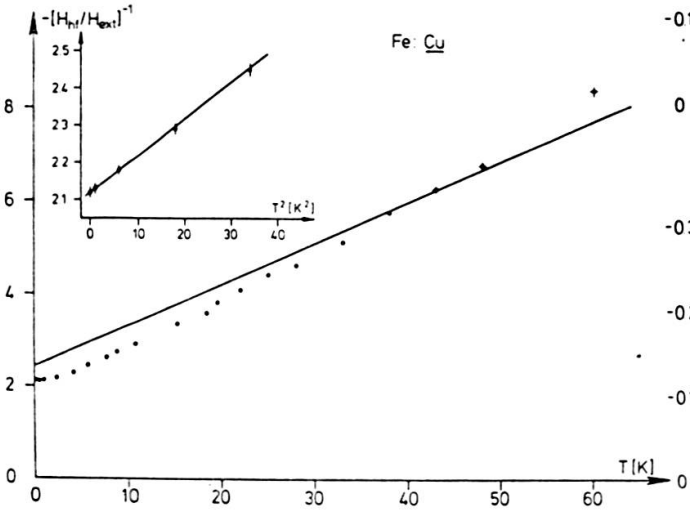


Fig. 3 c

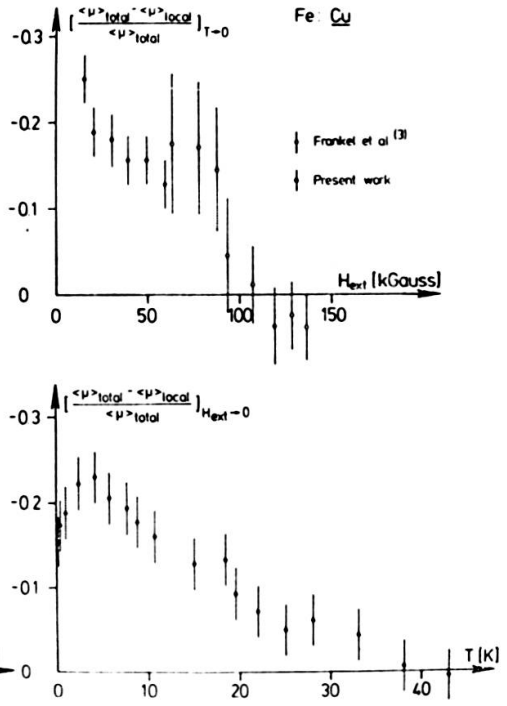


Fig. 3 d

FIG. 3.

a) Mössbauer spectra of ^{57}Fe in *Fe:Cu* for various external fields at $T = 30\ mK$.
b) Local susceptibility in *Fe:Cu* as function of the total susceptibility (from ref. 14 and 15).
c) Reciprocal local susceptibility in *Fe:Cu* as function of temperature.
d) Conduction electron polarization as function of external field and temperature.

of *Fe :Cu*. A set of typical spectra is shown in Figure 4a. In contrast to the *Fe :Cu* case the low temperature zero field spectrum shows a remarkable structure. All spectra could be fitted by taking broadening of the different transitions into account. Till now it is not clear, if this broadening is due to relaxation effects or due to a distribution of hyperfine fields by interaction between impurities. The hyperfine field of 93 (3) kG fitted to the zero-external field spectrum would favour the last assumption. The high temperature local susceptibility showed a small temperature independent part $H^L_{sf}/H_{ext} = 0.076\,(20)$, which may be attributed to an orbital contribution to the hyperfine field. In the following we correct the hyperfine fields for this contribution getting the spin part H^s_{hf} of the hyperfine field.

Figure 4b shows H^s_{hf} as function of the external field for various temperatures, including the $H_{ext} = 0$ values. From these curves we determined the initial local susceptibility $-\left[\Delta H^s_{hf} / \Delta H_{ext}\right] \mathrm{H}_{ext \to 0}$. At high temperatures $T > 15\,K$ we get a Curie Weiss law with $\theta_1 = 10\,K$ (Fig. 4c) in agreement with the magnetization data of Hurd [14] with a proportionality constant of $-\,115\,(10)\,kG/\mu_B$. At lower temperatures a Curie Weiss behavior with $\theta_2 = 0.5\,K$ and only $-\,78\,(10)\,kG/\mu_B$ is obtained again in agreement with low temperature magnetization data [18, 19]). In addition the local magnetization below 4.2 K is a linear function of the total magnetization [19] for external fields up to 60 kG again with $-\,85\,(3)\,kG/\mu_B$. At about $T_M = 0.5\,K$ the reciprocal initial susceptibility has a minimum, indicating some kind of antiferromagnetic order. The $H_{ext} = 0$ hyperfine fields extrapolate to zero about the same temperature.

We analysed the linebroadening in terms of two contributions: 1) a distribution of the hyperfine fields, assumed to be Lorentzian with a half width ΔH_{hf}; 2) broadening by relaxation effects with isotropic relaxation and $T_1 = T_2$, giving T^{-1}_{1e} for the excited 3/2 state in ^{57}Fe. For fields $H_{ext} \leq 10\,kG$ ΔH_{hf} (Fig. 4d) shows a maximum at about 0.5 K, again indicating some kind of magnetic ordering in this temperature regime. At higher fields ΔH_{hf} is nearly temperature independent ($\Delta H_{hf} \approx 10\,kG$) and vanishes for $T > 10\,K$. In each case ΔH_{hf} has a maximum at about the temperature, where the differential susceptibility is largest. At low fields $H_{ext} \leq 10\,kG$ the relaxation rate T^{-1}_{1e} (Fig. 4d) is strongly temperature dependent. For higher fields $H_{ext} \leq 20\,kG$ it is nearly zero ($T^{-1}_{1e} < 0.1\ Mc/s$). The hyperfine field H^s_{hf} as a function of H_{ext}/T is shown in Figure 4e. The typical Kondo behavior with the decrease of the saturation field with decreasing external field at low temperatures is clearly seen.

The data presented here would favour the picture that the Kondo temperature for this system is high ($\theta = 10\,K$) and that the low temperature and low field behaviour is essentially ruled by an antiferromagnetic interaction between impurities, giving rise to some kind of antiferromagnetic order near 0.5 K. This interpretation may be compared with recent data of Borg and Kitchens [20]. They deduce from Mössbauer and magnetization data of higher concentrated *Fe :Au* alloys ($100\,ppm \leq c \leq 18\,\%$),

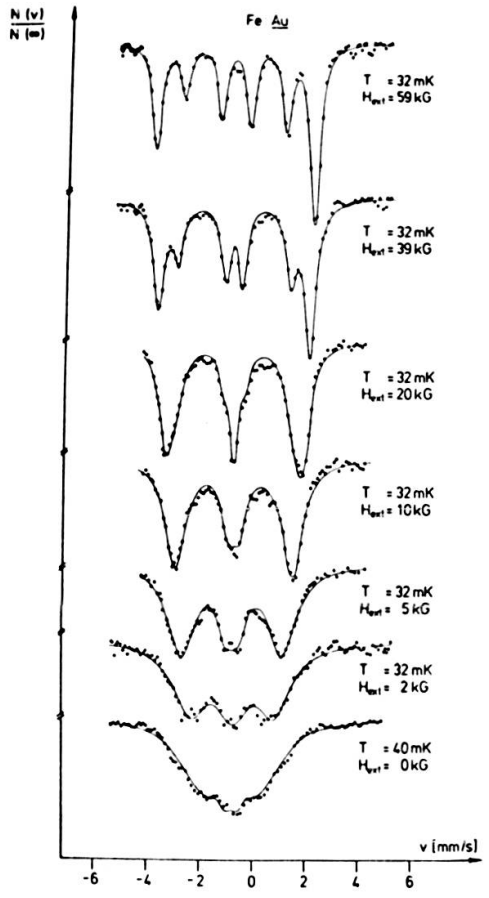


Fig. 4a

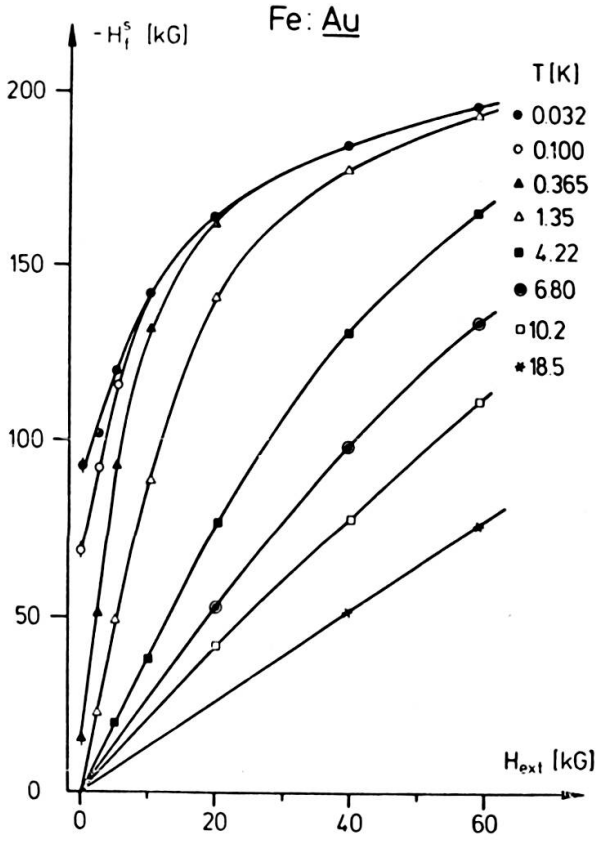


Fig. 4b

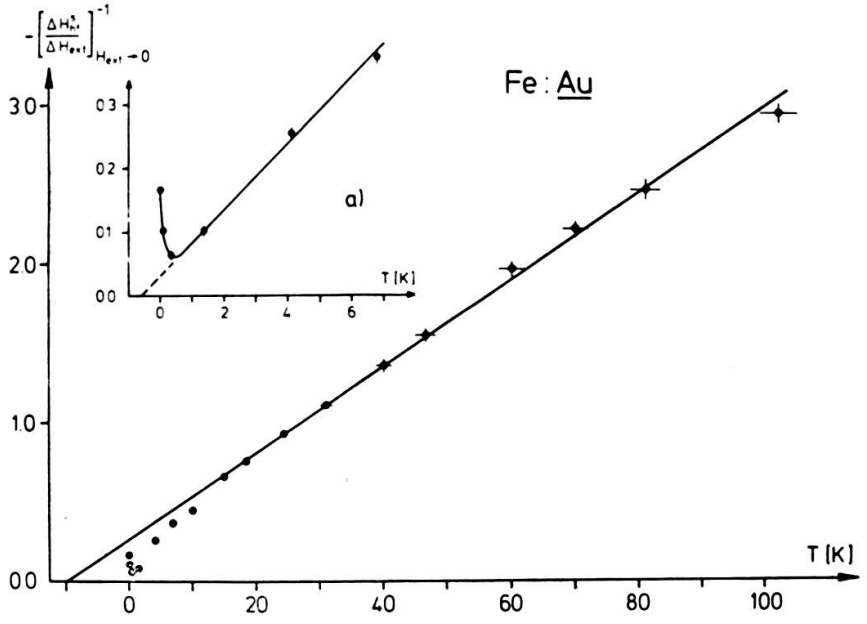


Fig. 4 c

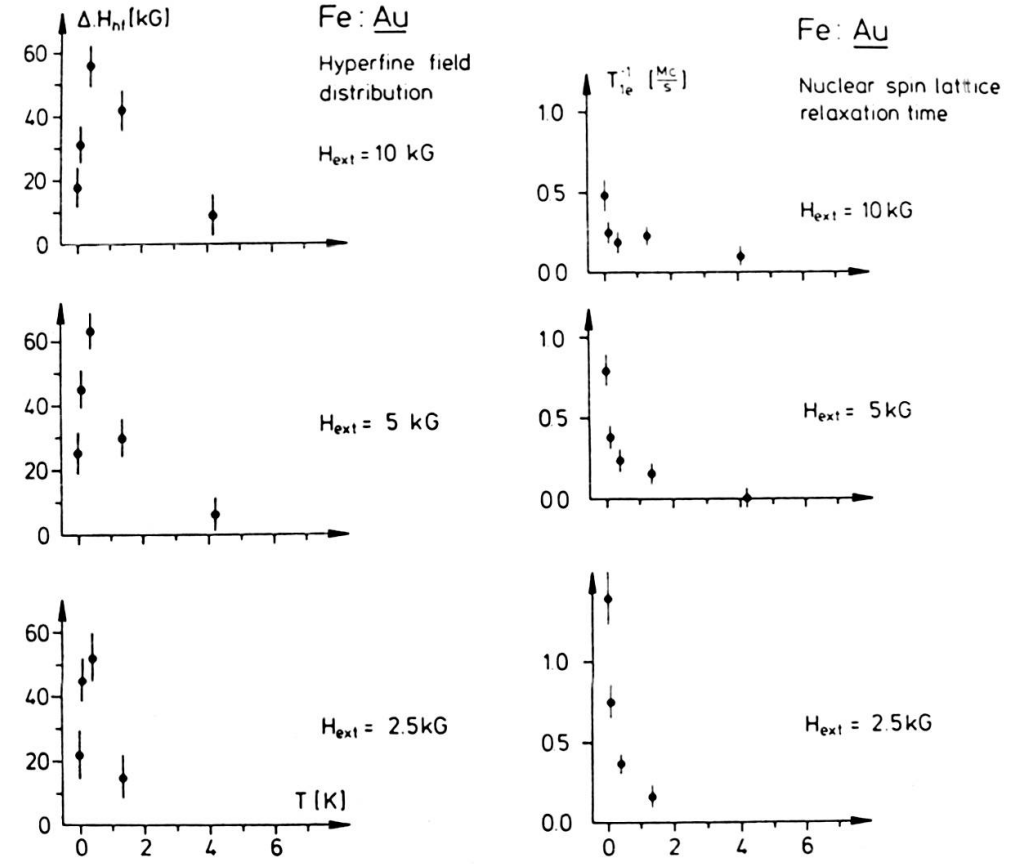


Fig. 4 d

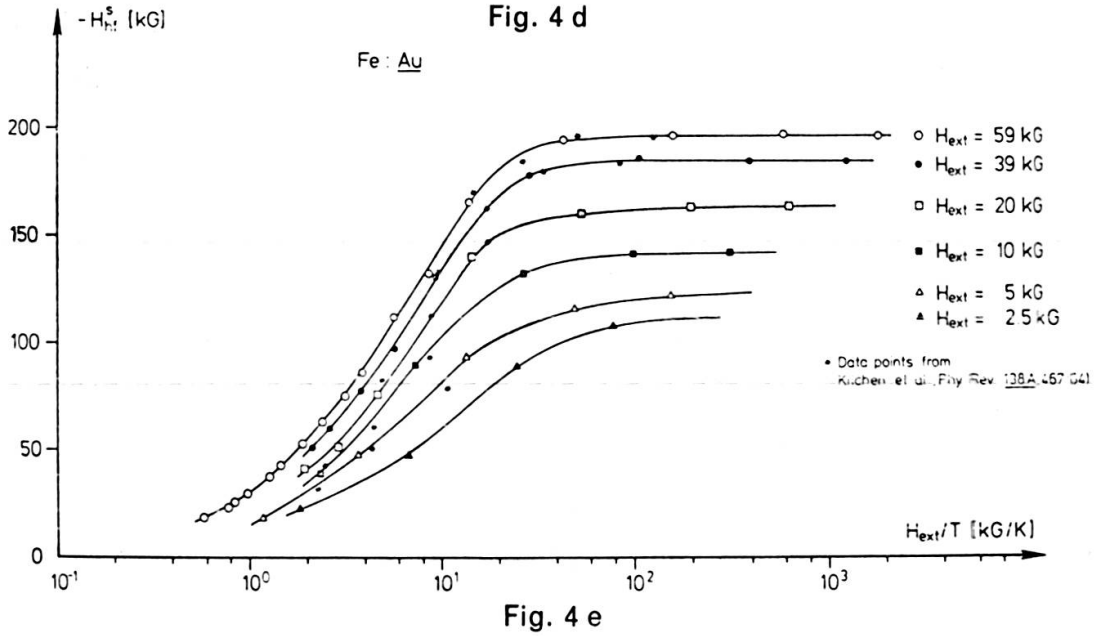


Fig. 4 e

FIG. 4.

a) Mössbauer spectra of ^{57}Fe in *Fe:Au* at various external fields at $T = 32\ mK$.

b) Spin contribution H^{s}_{hf} to the hyperfine field for *Fe:Au* as function of external field and temperature.

c) Reciprocal initial local susceptibility for *Fe:Au* as function of temperature.

d) Hyperfine field distribution ΔH_{hf} and nuclear relaxation rate T^{-1}_{1e} in *Fe:Au* for various external fields as function of temperature.

e) Local polarization in *Fe:Au* as function of H_{ext}/T for various external fields.

that at low concentrations the alloys order antiferromagnetically with $T_M \approx 1\,K$ for the $100\,ppm$ alloy. Also recent low field AC susceptibility measurements by Canella and Mydosh [21] show a very sharp minimum in the reciprocal susceptibility at low temperatures for samples with $c > 100\,ppm\,Fe$. The nominal magnetic impurity concentration for our source was $c < 10\,ppm$, but according to the preparation process (electroplating of carrierfree ^{57}Co activity to an Au foil with following diffusion and quenching) clustering of the activity in more concentrated parts is not unlikely. According to the relation $T_M = 11.6 \cdot x^{0.45}$ (x in at % Fe) given by Borg and Kitchens [20] a $10\,ppm\,Fe:Au$ alloy would already order at about $0.4\,K$. To understand the influence of Fe-Fe and Fe-Co interactions in Au clearly more experiments at low concentration and low temperatures are needed.

LOCAL MOMENTS IN A SUPERCONDUCTOR: Eu_xLa_{1-x}

At least I will shortly demonstrate the microscopic observation of magnetic ordering of the local Eu moments in the superconductor Eu_xLa_{1-x} [6]. Similar experiments were performed by Taylor *et al.* [22] on ^{57}Fe in $Ce_{1-x}Gd_xRu_2$. We studied the system Eu_xLa_{1-x} with Mössbauer experiments on ^{151}Eu using an unsplit source of $^{151}Sm_2O_3$ at a constant temperature and a Eu_xLa_{1-x} absorber ($x = 1.2$ at % and $x = 1.3$ at %) in the mixing chamber of the He^3/He^4-dilution refrigerator. The alloys became superconducting at about $2\,K$ and remained superconducting down to the lowest temperatures. Typical Mössbauer spectra for $x = 1.2$ at % are shown in Figure 5a. At low temperatures a typical magnetic hyperfine spectrum is observed. At higher temperatures the splitting decreases and the line width increases. Above $700\,mK$ the line width again decreases being temperature independent above $2\,K$. From the temperature dependence of the hyperfine splitting we got the temperature dependence of the local Eu moment in the superconducting state as shown in Figure 5b. The data fit very well to a magnetization curve of a spin 7/2 in a molecular field corresponding to the $S_{7/2}$ ground state of the Eu^{2+} ion. Further experiments to determine the concentration dependence of the magnetic ordering temperature in the superconducting state are in progress.

CONCLUSION

The presented examples show, that in certain cases (long relaxation limit) Mossbauer experiments give results similar to ESR. The advantage of the Mössbauer technique is, that the experiments can be performed in zero external fields. The analysis of the relevant local moment relaxation data from the Mössbauer spectra may however be much more complicated than for ESR experiments. In addition even at high local moment relaxation rates Mössbauer data show the behavior of

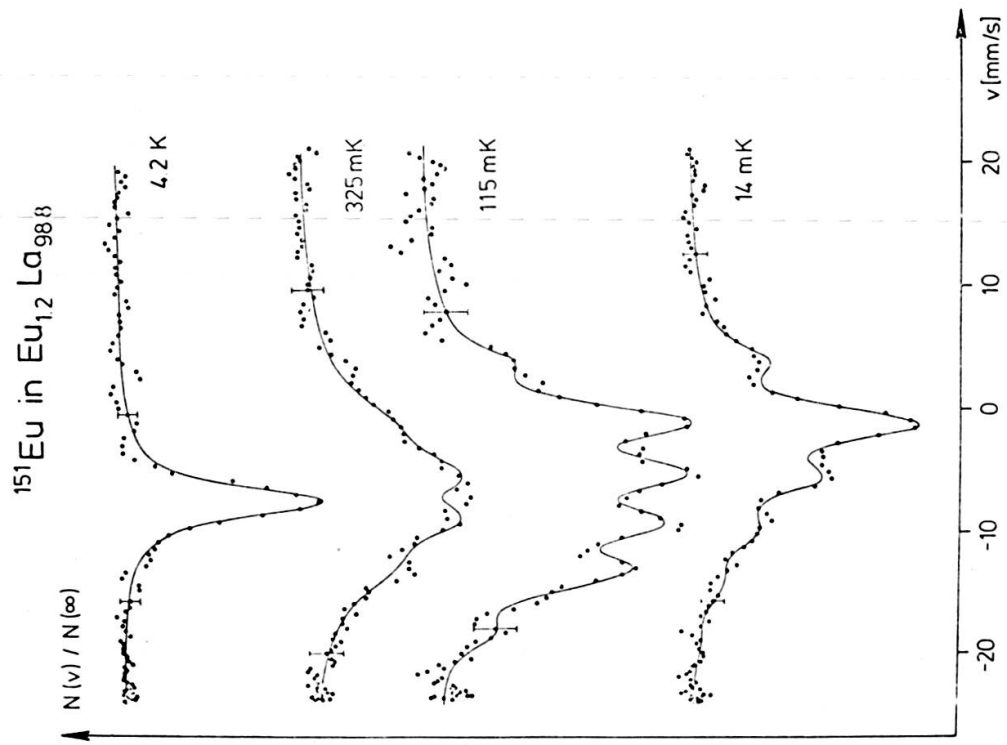


Fig. 5 a

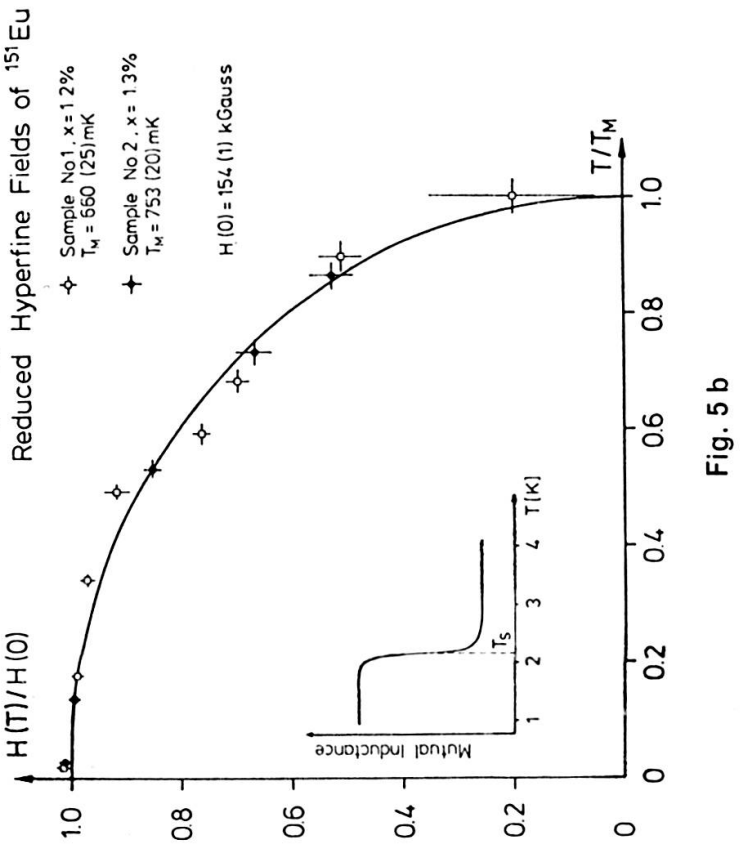


Fig. 5 b

FIG. 5.

a) Mössbauer spectra of ^{151}Eu in Eu_xLa_{1-x} with $x = 1.2$ at %.

b) Reduced hyperfine fields as function of reduced temperature for Eu_xLa_{1-x} (Insert: superconducting transition ofr the 1.2 at % scample).

the average local magnetization as function of external field and temperature, and therefore give direct evidence for magnetic ordering of the local moments by interactions between the impurities.

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DISCUSSION

HIRST: There is a different possibility of interpreting the *FeCu* results. You are thinking of an orbital contribution which is independent of T, which would be the case if you had an orbital singlet. The alternative possibility which would correspond to the interpretation I gave for the *EPR* would be that you start with an orbital degree of freedom and then assume strong spin-orbit coupling as

a first aproximation. You could perhaps have some tendency to break down this spin-orbit coupling which could give some correction terms. You can fit the data in this way, getting a reasonable fit for the susceptibility. Essentially it is the same picture you have, except that the spin is now a fictitious spin. The nice thing that comes out is that this fixctitious spin consists of both spin and orbital moment, and the orbital moment tends to cancel the hyperfine field from the spin because the hyperfine coupling constants are of opposite sign. This enables one to understand why it is that the hyperfine coupling constant for iron is relatively small compared for example to manganese. However, I must admit there is a difficulty with this, and that is I do not understand how it works for the case of iron in gold. Here one apparently does not see this cancellation. We do not have any *EPR* data for this system so it is impossible to check this assignment of the state.

STEINER: Okay. I must say we only looked for this temperature independent contribution due to an orbital moment, and we cannot distinguish the temperature dependence from the measurements. It could be done only if we could find this dependence in the total susceptibility too, then we could separate the various contributions.

HIRST: I think the main point in your analysis would not be changed very much if you interpret it that way, you just have a fictitious spin instead of a true spin.

STEINER: You think this deviation at lower temperatures could be due to the temperature dependence of this orbital contribution?

HIRST: It is plausible. I have not checked it in detail, but it is possible you would get such contributions from the breakdown of the spin-orbit coupling.

IMBERT: I would like to comment on the use we have made of the Mössbauer technique to study the Kondo anomaly of *AuYb*. We first use *Tm* in place of *Yb*; *Tm* has a non-magnetic ground state, and its solubility in *Au* is very good. An advantage of the Mössbauer technique is that we have a very good check on the good dilution of the impurity in the metal, since the Mössbauer effect is very sensitive to the local symmetry. What we observe is that when we lower the concentration we decrease normally the static broadening of our lines, but we observe a relaxation rate which is independent of the concentration. In other words I think concentration effects give rise first to a static broadening before giving a contribution to the relaxation.

Another point is that in a certain way it would be surprising not to see this negative slope of the relaxation rate over *T vs.* In *T* because according to perturbation theory this slope must represent the cube of the exchange constant, and this is known to be large and negative according to the measurements of Orbach and Davidov.

ORBACH: You must be a little careful because of the wave-vector dependence of the exchange. The *g*-shift and the linewidth and the Kondo terms all have different weightings. I am not arguing with you but be careful about taking the *g*-shift *J* value.

GONZALEZ: I would like to point out that in our experiments when we approach the hyperfine separation we can have another window in measuring the relaxation rates, that is the populations of the levels.

HIRST: You mean the differential populations of the hyperfine levels?

GONZALEZ: Yes. We have non-equilibrium populations which allow us to measure the relaxation rate. This is good for the *AuYb* alloys where the relaxation rate is near the inverse lifetime of the hyperfine separation. This is another window founded in a completely different principle to that of the line shape method which is valid when you have slow relaxation.