Susceptibility of Fe in Cu

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(Received 9 July 1974)

The Mössbauer effect of *Cu*:Fe has been measured for 30 mK $< T <$ 100 K in external fields up to 60 kG. A constant temperature-independent term is subtracted from the hyperfine fields. After this correction the local susceptibility is in agreement with bulk magnetization, neutron diffraction, and NMR data. At the very lowest temperatures the local susceptibility becomes temperature independent, in agreement with theoretical expectations.

INTRODUCTION

For insulators, the study of dilute impurities of ions carrying a magnetic moment has contributed considerably to the understanding of concentrated ionic magnetic systems. The same approach has led in metallic systems, to more complications than anticipated, which are generally described by the name Kondo effect.[1,2] In brief, that means that, in the case of antiferromagnetic coupling of the magnetic moment to the conduction electrons, below a certain temperature anomalies in various properties are observed as, e.g., a minimum in the electrical resistivity or a maximum in the specific heat. The solution of this problem is difficult on the theoretical side as well as on the experimental side. Theoretically it involves the solution of a complicated many-body problem and therefore only approximate solutions are available at this point. Experimentally it has been found that one has to go to very small concentrations of the magnetic impurities in order to observe effects which are really due to the coupling of a single spin to the conduction electrons and not effects produced by clusters of spins. This poses considerable metallurgical problems and also problems in the measuring accuracy.

The theoretical effort has recently yielded solutions for the susceptibility.[3] There is therefore an especially important need for accurate experimental data to check these theoretical predictions. A special problem which has led to some controversy is the question of the nature of the ground state. Experimental and theoretical work of some groups[2,4–6] seemed to indicate that the ground state is a correlated many-body singlet between the impurity spin and the conduction electrons. This many-body ground-state quasiparticle is clearly evident only in the susceptibility data. It leads to a difference in the total susceptibility (spin and conduction electrons) as compared to only the spin susceptibility (local susceptibility). Other work, theoretical[7–9] and experimental,[10–12] does not yield this ground state and therefore does not result in any difference of the total and the local susceptibility. Mössbauer-effect experiments[13,14] have played a considerable role in setting up this quasiparticle picture, and in order to throw some light on the situation, the present series of experiments using the Mössbauer effect of *Cu*: Fe was performed.[15,16]

The value of hyperfine measurements in determining the susceptibility has recently been discussed thoroughly by Narath,[17] and we do not want to go into the details here. It is sufficient to remark that there is every evidence that the temperature dependence of the Knight shift or—to put it in other words—of the hyperfine field really represents the temperature dependence of the susceptibility; since the hyperfine data are often of reasonable precision, these types of measurements therefore represent an accurate determination of the temperature dependence of the susceptibilities. Unfortunately, the Knight shift, especially in transition-metal ions, also contains a temperature-independent term which comes from an orbital contribution to the magnetic moment. It is this contribution which has to be subtracted from the total Knight shift to obtain the *d*-spin Knight shift in which one is interested. The subtraction of this contribution sometimes presents considerable problems.

Mössbauer experiments on the system Fe in Cu have been performed before by two groups.[13,14] Since these experiments have been used as experimental evidence for the existence of the singlet ground state it was decided to repeat these experiments and extend them in order to clarify the situation. First results of these experiments were published in previous communications.[15,16] In the present analysis new results for the temperature range 60–100 K are included.

EXPERIMENTS

The previous experiments using the Mössbauer effect[13,14] still had considerable error presumably owing to problems in accumulating the necessary statistics for data of high accuracy. It was therefore one of the prime efforts in the present investigation to increase the statistical accuracy considerably. In addition, it seemed interesting to

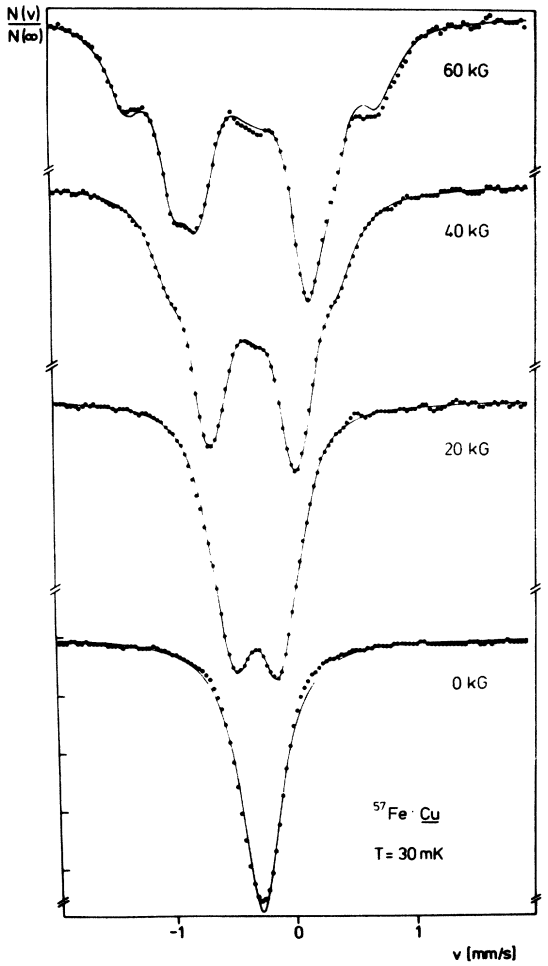

FIG. 1. Mössbauer spectra with a source of ^{57}Fe in Cu at 30 mK for various external fields. The single-line potassium-ferrocyanide absorber was at a constant temperature of 1.3 K and experienced the same external field as the source parallel to the γ beam.

reach larger H/T values, which in a laboratory experiment is most easily achieved by going to lower temperatures. The present experiments were performed in a He^3/He^4 dilution refrigerator with a source of about 1-mCi ^{57}Co diffused into Cu. This source reached a temperature of about 30 mK at most. The source was prepared by electroplating the carrier-free ^{57}Co onto pure Cu and by diffusing the Co into the Cu in a hydrogen atmosphere. The estimated impurity concentration was less than 10 ppm. An autoradiography of this source showed a rather homogeneous distribution of the radioactivity. At room temperature the source produced a linewidth of 0.22 mm/sec with a thin single-line absorber of potassium ferrocyanide, indicating that there was only a little clustering in the source. Magnetic fields parallel to the observation of the 14-keV γ rays up to 60 kG could be produced with a superconducting solenoid. In order to increase the counting statistics and to avoid undefined stray fields at the absorber, it was decided to place the source and the absorber, which was held at a constant temperature of about 1.3 K, in the same magnetic field, which produces a very favorable geometry. In addition, a thick absorber of potassium ferrocyanide enriched in ^{57}Fe was used in order to increase the statistical accuracy, resulting in a linewidth of 0.34 mm/sec at 300 K and 0.39 mm/sec from 4.2 K down to 30 mK. The temperature could be varied between 30 mK and approximately 100 K by heating with a resistance. The temperature measured with a carbon resistor was calibrated with various superconducting transition points and also by observing the polarization in a Mössbauer experiment with ^{151}EuS. Temperatures below 100 mK were determined self-consistently by the polarization seen in the Mössbauer spectra, using the known Knight shift of 5% of Co in Cu.[17] The accuracy of the temperature calibration was about 3% and did not by any means influence the significance of the results. A number of spectra are shown in Figs. 1 and 2. These spectra do not show a usual six-line pattern because they represent a folding of two magnetically split spectra. But as the splitting is well resolved it is of course easy to deconvolute the spectra or to determine the interesting parameters, which are the hyperfine field in the source and the internal field in the absorber which calibrates the external field. All the spectra were fitted with Lorentzian lines, where the splitting is given by the external field and the hyperfine field in the source. The relative intensities of the lines were taken from the theoretical expression for a quantization axis parallel to the γ beam. At low temperatures the asymmetry in the line intensities due to the polarization in the ^{57}Co parent state was taken into account. In addition, owing to the large effective thickness of the absorber ($T_{eff} \approx 7$) a small correction term for the intensity and linewidth of the strongest absorption lines was added to the program. The determination of the hyperfine fields with reasonable accuracy from the spectra with structure then presents no problem. On the other hand, in the regime above 30 K the hyperfine fields get very small even in the highest available external field of 60 kG. The three main peaks which result from the splitting of the absorber and of the source in the external field alone are only broadened by the hyperfine field in the source. Computer simulations using the exact transmission integral with reasonable values for the linewidths of source and absorber and the effective thickness of the absorber, however, showed that for an external field of 60 kG the source hyperfine field can be obtained from the data with an accuracy of 0.2–0.3 kG up to temperatures of about 100 K at which temperature the source hyper-

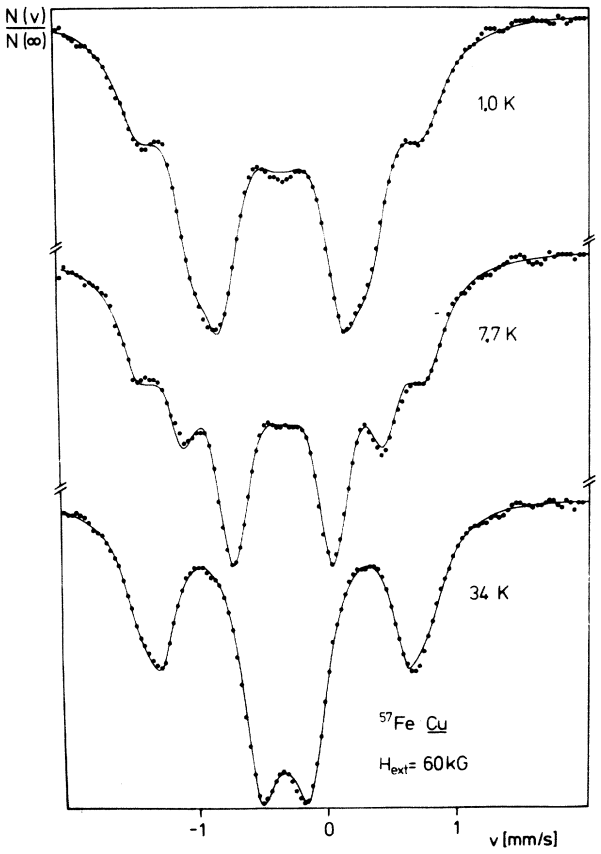

FIG. 2. Mössbauer spectra with a source of ^{57}Fe in Cu in a field of 60 kG parallel to the γ beam for various temperatures. The absorber was potassium ferrocyanide at a temperature of about 1.3 K in the same field of 60 kG.

fine field is about 3 kG. The experimental data are listed in Table I. At temperatures above 0.1 K the hyperfine fields H_{hf} were found to be a linear function of the external field H_{ext} up to $H_{ext} = 60$ kG. At higher temperatures therefore only the $H_{ext} = 60$ kG value was measured to determine the initial local susceptibility. In Table I the external fields have always been normalized to the full decimal value in order to make a comparison simpler. The correction from the actually measured value was easily done because of the linearity of the hyperfine field as a function of the external field.

INTERPRETATION OF EXPERIMENTAL RESULTS

The interpretation of the experimental magnetic data has often yielded confusion in the magnetic-impurity field because one tried to fit various theoretical expectations to the data. On the other hand, it is often not clear what the various contributions to the measured properties are and how they can be disentangled. In the present paper we shall therefore try to proceed in this direction very conservatively.

In order to compare the hyperfine field, which is the same property as the Knight shift with macroscopic susceptibilities, one has therefore to inspect carefully which contributions are contained in the Knight shift. In principle the susceptibility and also the Knight shift contain two terms[17]: one which comes from the spin magnetic moment and another one which comes from the orbital magnetic moment. These two terms have a different temperature dependence. Assuming an orbital singlet ground state the spin part of the susceptibility obeys a Curie-Weiss law, whereas any orbital contribution to the susceptibility should be essentially temperature independent. This is the generally accepted interpretation of the temperature-dependent and temperature-independent parts of the local moment susceptibility. If the spin-orbit coupling is included in the consideration, then also for an orbital singlet ground state some orbital character can be admixed to the temperature-dependent Curie-Weiss term and a spin contribution to the Van Vleck term. As the corresponding hyperfine coupling constants are normally different these contributions would show up differently in the hyperfine data and bulk magnetization data, respectively. But so far there is no definite evidence for a measurable effect of this

TABLE I. Hyperfine fields in kG for ^{57}Fe in Cu, T in k.

	H_{ext}				
T	60	50	40	30	20
0.037	−28.0(2)	−23.9(2)	−19.2(2)	−14.4(2)	−9.6(3)
0.041	−28.3(2)	−24.2(2)	−19.1(2)	−14.7(2)	−9.9(3)
0.047	−28.1(2)		−19.6(2)		
0.069	−28.0(2)				
0.071	−28.2(2)				
0.100	−28.3(2)	−24.1(2)	−19.1(2)	−14.1(2)	−9.9(3)
0.410	−28.4(2)	−24.0(2)	−19.2(2)	−14.0(2)	−9.9(3)
1.00	−28.1(2)	−24.1(2)	−19.0(2)	−13.9(2)	9.7(3)
2.45	−27.5(2)	−23.6(2)	−18.8(2)	−14.0(2)	−9.8(3)
4.22	−26.2(2)	−22.3(2)	−18.3(2)	−13.3(2)	−9.6(3)
5.80	−24.5(2)				
7.70	−23.0(2)				
8.80	−22.0(2)				
10.7	−20.6(2)				
12.0	−19.7(2)	−16.7(2)	−13.6(2)	−10.2(3)	
12.6	−19.5(2)				
15.2	−17.9(2)				
15.7	−17.8(2)				
18.4	−16.7(2)				
19.5	−15.8(2)				
22.0	−14.7(2)				
25.0	−13.6(2)				
26.7	−13.5(2)				
28	−13.0(2)				
30	−12.6(2)	−10.7(3)	−8.5(3)		
33	−11.7(2)				
38	−10.4(2)				
43	−9.6(2)				
46	−9.1(2)				
48	−8.9(2)				
55	−7.7(2)				
60	−7.1(2)				
64	−6.4(2)				
72	−5.9(2)				
78	−5.2(3)				
84	−4.7(3)				
94	−4.0(3)				
102	−3.6(3)				

latter contribution. It should be added that, of course, the spin hyperfine field contains parts due to conduction-electron and core polarization, but as far as we know they are all proportional to the thermal average of the spin itself and their temperature dependence is therefore proportional to that of the susceptibility. The small positive temperature-independent contribution from conduction electrons, polarized in the external field, can be neglected.[17] In order to study the temperature dependence of the spin susceptibility as determined from Knight shift or hyperfine studies it is therefore of extreme importance to subtract the temperature-independent part from it.[17] This temperature-independent part can contribute so largely to the hyperfine interaction because of the large enhancement factor of the orbital magnetic moment as compared to the spin magnetic moment. Therefore it is also usually very hard to detect it in the susceptibility measurements.

In principle, one can determine this temperature-independent part from the hyperfine fields by plotting the measured hyperfine fields as a function of $1/T$ and determining the $T=\infty$ intercept. In the present work we did not have data which extended over a far enough temperature regime to make this kind of analysis the most accurate one. Keeping in mind that the present data extend only to 100 K which is only about 3Θ (Θ is the Curie-Weiss intercept of the macroscopic susceptibility), it is hard to determine the high-temperature behavior from the hyperfine data alone. On the other hand, it seemed desirable to see what results the present data yielded alone. We shall therefore now present two analyses of the data, one using no other information than the Mössbauer data and the other performed in such a way that parameters are determined with the highest possible accuracy, which is possible only by also using other data.

Analysis A (most accurate)

In order to separate the spin and orbital contributions to the hyperfine field it was assumed that the spin contribution to the hyperfine field is proportional to the macroscopic spin susceptibility. At this point all the experimental evidence supports this assumption. The macroscopic susceptibility, being measured between 1 and 1000 K (Refs. 18–21), allows one to extract the Curie-Weiss temperature Θ with considerable accuracy. On the other hand, the orbital contribution to the macroscopic susceptibility is only small, as compared to the spin term. All available macroscopic susceptibility data were collected in order to determine the exact temperature dependence of the macroscopic susceptibility. Then this temperature dependence was used to plot the hyperfine data against them, and the plot was used to determine a possible orbital contribution to the hyperfine field. This procedure was also used by Narath in his analysis of the *Au*: V NMR data.[17] We have therefore fitted all the available macroscopic susceptibility data, extrapolated as well as possible to zero Fe concentration, to a function of the form

$$\lambda_{\mathrm{mac}} = \alpha_{\mathrm{mac}}/(T+\Theta_{\mathrm{mac}}) + \beta_{\mathrm{mac}} , \tag{1a}$$

where the index "mac" emphasizes the fact that we are dealing with the macroscopic data. In the temperature range below 10 K, where as shown in the work of Tholence and Tournier[19] interaction effects between the iron moments are most important, only the data from this careful analysis were used. This fit, indeed, revealed a small temperature-independent contribution to the total susceptibility. In addition it gave a Curie-Weiss temperature of 27.6 (1.0) K, a value which we think is superior to those quoted before because it is obtained by an analysis over a much wider temperature region and also uses data of different origin, which makes it likely that systematic errors in either one of the measurements have been reduced. From $\alpha_{\mathrm{mac}} = \mu_{\mathrm{eff}}^2/3k$ a value of $\mu_{\mathrm{eff}} = 3.54\ \mu_B$ is obtained. If a spin of $S = \frac{3}{2}$ is assumed this yields $\mu = [S/(S+1)]^{1/2}\ \mu_{\mathrm{eff}} = 2.74\ \mu_B$ or with $\mu = gS\mu_B$ a value of $g = 1.83$. The results of this procedure are shown in Fig. 3, and one sees that the data are very well represented over about three decades in temperature by a straight line. It should be pointed out here that there are essentially only three data points available below 10 K.

In Fig. 4 we have plotted all the hyperfine data as a function of the temperature dependence determined for the total susceptibility. If we take only our data that extend up to about 100 K it can be seen that, within experimental accuracy, they can be fitted with the straight line, except for the points at the very low temperatures below 10 K, where there is a leveling off to a constant value of the susceptibility, very similar indeed to the behavior found in the *Au*: V system.[22,23] This interpretation clearly has to disregard the high-temperature data of two previous groups,[13,14] which are, of course, of much less accuracy. At the present time we see no explanation for the discrepancy of our data with those of the previous experiments. If, on the other hand, we do include the data of the previous work in the analysis, the fit to a Curie-Weiss behavior is much worse and there is also a considerable extra contribution to the susceptibility at the lowest temperature.[15]

Analysis B (only present Mössbauer data)

In order to check the consistency of the present experimental results and to assure that the interpretation is not biased by the use of other data, we have also analyzed only the present data within the

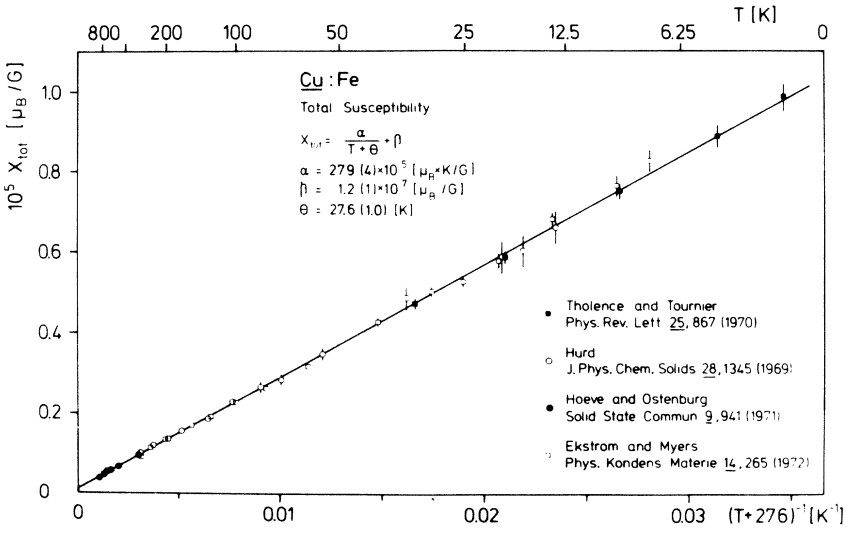

FIG. 3. Total susceptibility of Fe in Cu from bulk magnetization data as a function of $(T+27.6)^{-1}$ for $1.5 < T < 1000$ K.

approach outlined above. That is, the measured hyperfine fields H_{hf} were fitted to an equation of the form

$$\chi_{loc} = (\Delta H_{hf}/\Delta H_{ext})_{H_{ext}\to 0} = \alpha_{ME}/(T+\Theta_{ME}) + \beta_{ME}, \tag{1b}$$

with $H_{eff} = H_{ext} + H_{hf}$ and $\chi_{loc} = \chi_{ME}$.

H_{eff} is the effective field at the nucleus for ^{57}Fe in Cu, H_{ext} the applied field, and the index ME indicates that we are dealing with the Mössbauer-effect data. Clearly not all data points can be used in this procedure because of the leveling off of the susceptibility at the lowest temperatures. It was found that if only the data for $T > 15$ K were used, the normalized χ^2 of the fits were smaller than 1, whereas the fits deteriorated markedly in quality if points at lower temperatures were also included.

Then also the macroscopic data in the temperature range $15 < T < 1000$ K were fitted to Eqs. (1), and these data are included in Table II under analysis *B*. The results of the analyses *A* and *B* are compared in Table II.

It is apparent that within the statistical accuracy the results of the two analyses agree surprisingly well. This is support for the use of the hyperfine data in the magnetic-impurity problem.

From the constant values β_{ME} and β_{mac} we get a value of 470 kG/μ_B for the orbital part of the hyperfine field, in good agreement with theoretical estimates for Fe.[17] In Fig. 5 we have plotted the hyper-

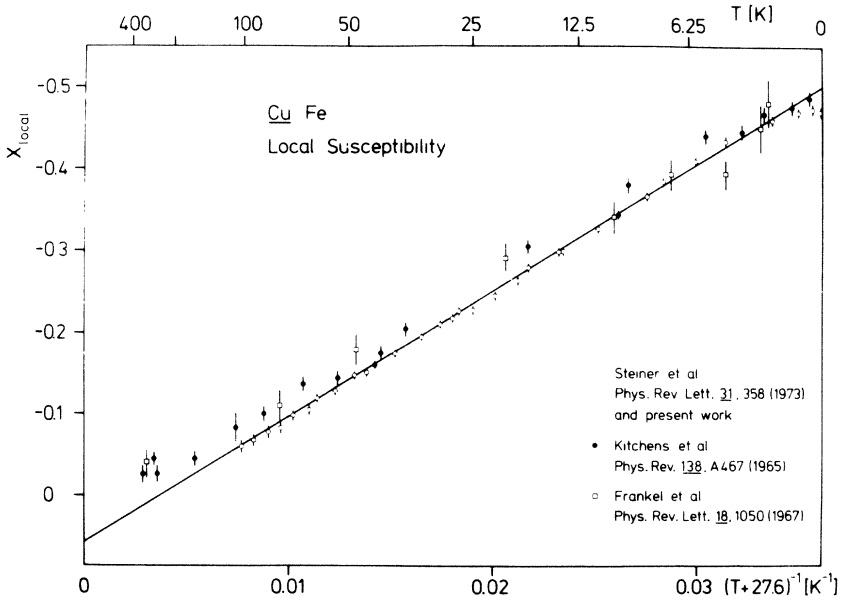

FIG. 4. Local susceptibility of Fe in Cu from Mössbauer experiments as a function of $(T+27.6)^{-1}$ for $0.03 < T < 100$ K.

TABLE II. Results of analyses A and B, described in the text. The index mac indicates the macriscopic magnetization results (Refs. 10–13) and ME indicates the Mössbauer results.

	α_{mac}	Θ_{mac}	β_{mac}	α_{Me}	Θ_{ME}	β_{ME}
Analysis A	27.6(4)	27.6(1.0)	0.012(1)	−15.3(2)	Θ_{mac}	0.057(2)
	$1.3 \leq T \leq 1000$ K			$15 \leq T \leq 102$ K		
Analysis B	27.9(4)	28.2(1.0)	0.012(1)	−15.2(1.2)	27.5(2.5)	0.056(9)
	$15 \leq T \leq 1000$ K			$15 \leq T \leq 102$ K		
Units	$10^{-5}\ \mu_B$K/G	K	$10^{-5}\ \mu_B$/G	K	K	

fine field H_{hf}, corrected for the orbital contribution term as obtained from analysis A, as a function of H/T. Henceforth the properties corrected for the constant orbital contribution will be designated with an additional index d in order to emphasize the fact that they are the d-spin contribution only. This plot is similar to that used by Frankel and his collaborators,[14] and the high-field data of these authors are also included in the Fig. 5. This way of displaying the data shows nicely the breaking up of the Kondo state, because for a free spin the hyperfine field should also always converge to the same value for large values of H/T. We have also plotted the behavior expected for a free spin in this graph, using $S = \frac{3}{2}$ and a g factor of $g = 1.83(2)$, as deduced from the Curie constant of the bulk susceptibility, and $H_{hf}^{d} = -101$ kG/spin (yielding $H_{sat}^{d} = -151$ kG), from a comparison of the local and total susceptibilities. This number is directly obtained from a plot similar to the one in Fig. 4, using the following relations:

$$H_{hf}^{d} = H_{sat}^{d}\langle S_z\rangle/S, \tag{2a}$$

$$\chi_{loc}^{d} = (H_{hf}^{d}/H_{ext})_{H_{ext}\to 0}, \tag{2b}$$

$$\chi_{mac}^{d} = g\mu_B(\langle S_z\rangle/H_{ext})_{H_{ext}\to 0}, \tag{2c}$$

$$\chi_{loc}^{d} = (H_{sat}^{d}/Sg\mu_B)\,\chi_{mac}^{d}. \tag{2d}$$

There again the deviation from the free-spin behavior can be seen. In Fig. 6 the inverse normalized spin susceptibility $\hat{\chi}^{-1} = \alpha/(\chi - \beta) = T + \Theta$ is shown as a function of T. This method of displaying the data allows the plotting of macroscopic and hyperfine data in one plot. The straight line is the Curie-Weiss behavior with a $\Theta = 27.6$ K, obtained from the macroscopic susceptibility measurements in analysis A. We have arbitrarily chosen this fit because it best represents the macroscopic and microscopic data. The lower insert in that Fig. 6 displays in greater detail the very-low-temperature part of the susceptibility, which clearly shows the leveling off to the constant value at the very lowest temperatures. This figure shows quite convincingly that at this point there is not really a difference in the functional behavior of the two susceptibilities. The data from the macroscopic experiments are unfortunately too scarce to show the leveling off at the lowest temperatures.

DISCUSSION

The Kondo effect is produced by ground-state spin correlations in the coupled-local-moment–conduction-electron system. The Mössbauer effect and nuclear resonance have so far only measured the spatial variation of the magnetization and thus the static susceptibility. The correlations can also contribute to the susceptibility, but it does not seem possible to derive the correlation function from the present experimental data.

The interpretation of the susceptibility of Fe in Cu has long been controversial. Mössbauer-effect data, nuclear-resonance data, and susceptibility data had been used originally to formulate the idea of the quasiparticle in the Kondo state.[2,4] This

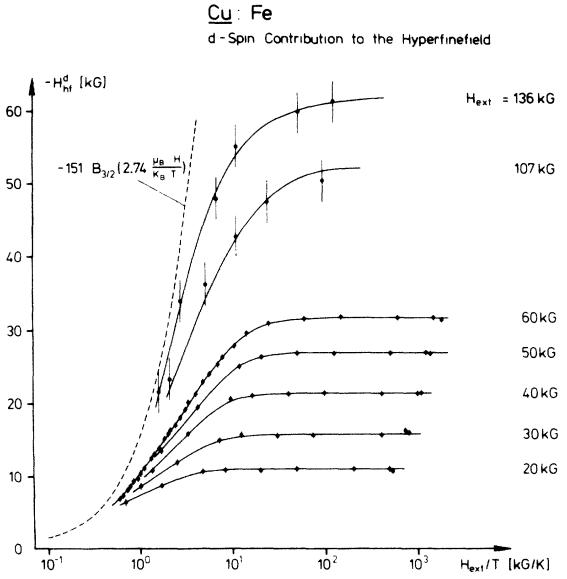

FIG. 5. d-spin contribution to the hyperfine field of ^{57}Fe in Cu from Mössbauer experiments as a function of H_{ext}/T for various external fields. $H_{ext} = 136$ and 107 kG taken from Frankel *et al.*, Phys. Rev. Lett. 18, 1052 (1967).

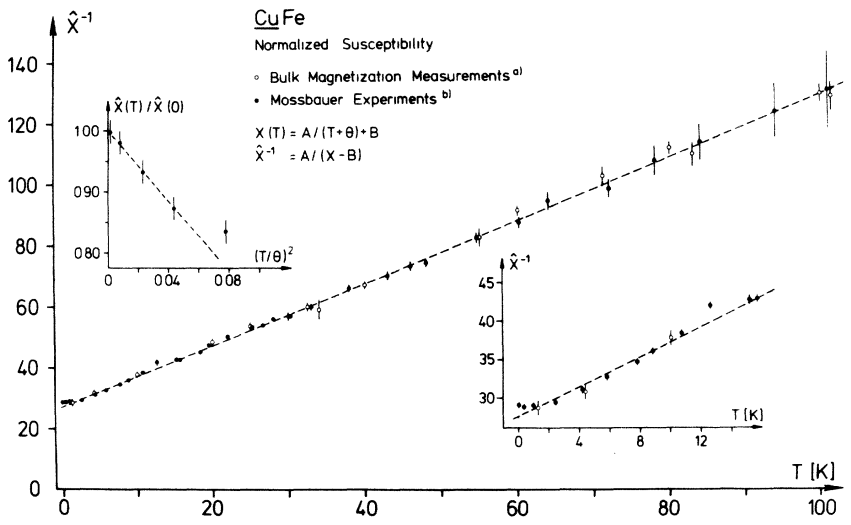

FIG. 6. Reciprocal d-spin susceptibility for Fe in Cu from bulk magnetization data from Refs. 19–21 (total susceptibility) and Mössbauer data (local susceptibility) as function of temperature for $T < 100$ K. The susceptibilities are normalized to the corresponding Curie constant α. The lower insert shows the saturation at lower temperatures while the upper insert displays the T^2 law for $T/\Theta < 1/5$.

consisted essentially of a correlated state of the impurity spin and a spacially extended ferromagnetically coupled conduction-electron cloud. This results in a deviation of the local (impurity spin) susceptibility from the total susceptibility [(impurity spin) + (conduction electron)]. Neutron diffraction data,[14] which in principle are the most elegant way to probe the spatial dependence of the spin polarization, could not confirm the suggestion of the early interpretation. A careful analysis of the macroscopic susceptibility[19] showed then that much of the susceptibility at temperatures comparable to the Kondo temperature was actually due to clusters of two and more Fe ions and not representative for a single-impurity behavior. The single-impurity susceptibility showed then a Curie-Weiss behavior down to 1.3 K. In the light of these findings it was then proposed that the effects which were originally attributed to the quasiparticle did indeed result from an effect of the Fe clusters.[24] More careful Mössbauer effect measurements[15] over a wider temperature range did not seem to confirm this suggestion. If they were combined with the old Mössbauer data,[13,14] there resulted an extra contribution to the local susceptibility as compared to the total susceptibility which could be interpreted in terms of the quasiparticle, although its amplitude was reduced as compared to the old analysis and had the opposite sign. In addition, the first analysis of the new Mössbauer-effect data neglected an orbital contribution to the hyperfine field which enhanced the quasiparticle amplitude.

Nuclear-resonance experiments[12] on the Knight shift seen by Cu ions which were neighbors to Fe impurities, did not show any deviation from the temperature dependence found in the macroscopic-susceptibility measurements and resulted therefore in a blow to the quasiparticle picture. The present Mössbauer-effect measurements alone show, after an analysis taking into account a constant term from the orbital hyperfine field, the same temperature dependence of the susceptibility as the macroscopic experiments. The Mössbauer-effect data are therefore in agreement with the neutron-diffraction experiments[11] and with the recent nuclear-resonance experiment.[12]

A careful inspection of Figs. 5 and 6 shows that the situation is by no means completely satisfactory. First of all, the data of the present series of experiments and those of the earlier measurements[13,14] disagree outside their errors. At this point we can offer no convincing explanation for this disturbing situation. Second, the low-temperature data ($T < 10$ K), even of the present series of experiments, seem to indicate a trend to deviate from the line that is given by the temperature dependence of the macroscopic magnetic data. This deviation is not really large enough to be statistically significant, but it remains a point of concern.

At this point the other available information on a possible nonzero spin polarization of the electron gas in the Kondo state has to be inspected. The only other experimental information comes from the NMR measurements on *Cu*: Co from Slichter's[28] group. They measure the Knight shift of three sorts of Cu neighbors of the Co ions. From these Knight shifts the conclusion is reached that there is a nonzero spin polarization of about 7%, coupled antiferromagnetically to the impurity spin. Yet there is a peculiarity in the *Cu*: Co data which leaves this system open to discussion. The temperature dependence of the satellite Knight shift yielded, if fitted to a Curie-Weiss law, an intercept of $\Theta = 4700 \pm 1000$ K, very different from that found for the total susceptibility ($\Theta = 950 \pm 100$ K). If a quadratic temperature dependence of the form $1/\chi \propto 1 + (T/1.2\Theta)^2$

is fitted to these data this still yields only 1600 K for Θ. This difference in the temperature dependence for the total and the local susceptibility in the *Cu*: Co system is at present unexplained and requires further investigation. The theoretical investigations of the question of a nonzero spin polarization also yield different results. The work of Bloomfield *et al.*[29] predicts a small nonzero polarization, coupled antiferromagnetically to the impurity spin. The calculations of other authors[7,8] give no such polarization, whereas the calculation of Heeger *et al.*[5] then give a polarization which has the same order of magnitude as the impurity-spin polarization, but which is also coupled ferromagnetically to the impurity spin. Unfortunately, all these theories give a divergent susceptibility at $T=0$, which shows their deficiencies. The recent theoretical efforts[3] which have removed that divergence in the susceptibility have not yet calculated the spin–conduction-electron correlation function.

The present experimental findings rule out the prediction of a large temperature-dependent ferromagnetic-spin polarization but cannot distinguish between a small and a zero polarization. In the present data a small deviation of the local susceptibility from the total susceptibility cannot really be detected because the macroscopic data are not sufficiently detailed at low temperatures. So the present data cannot rule out a polarization of the size of a few percent of the impurity susceptibility.

The present Mössbauer-effect data also show the leveling off of the susceptibility for $T \ll \Theta$ expected from recent theoretical predictions.[3] For *Cu*: Fe this type of behavior was first found by Triplett and Phillips[25] from a measurement of the magnetic-field dependence of the low-temperature specific heat, and was interpreted as evidence of a nonmagnetic ground state in that system. This low-temperature leveling off of the susceptibility was also found previously for the *Au*: V system.[22,23] It therefore seems that the experiments on *Au*: V and on *Cu*: Fe, which are perhaps the two most thoroughly studied over a large temperature range above and below the characteristic Curie-Weiss temperature Θ, yield a coherent picture as far as their magnetic behavior is concerned. They show a Curie-Weiss behavior for the susceptibility at high temperatures. For temperatures far below the Curie-Weiss temperature the susceptibility becomes temperature independent. In addition, in both systems the temperature dependence of the total susceptibility $\chi^d_{\rm loc}$ of the impurity spin seems to have the same functional dependence, which seems to remove the experimental basis for the formulation of the quasiparticle picture. As mentioned the very-low-temperature ($T \ll T_K$) susceptibility of the Kondo alloys seems to be described by a relation of the type

$$\chi(T)/\chi(T=0) = 1 - a(T/\Theta)^2 \qquad (3)$$

shown in the upper insert of Fig. 6. *Au*: V and *Cu*: Fe are the only systems which, as far as we know, have been measured over a large temperature range, so that it is possible to determine Θ from the data for $T > \Theta$ and a and $\chi(T=0)$ from the data with $T \ll \Theta$. The T^2 behavior has also been found in *Al*: Mn,[27] and perhaps in *Cu*: Co.[28] But in these systems the Curie-Weiss temperature Θ is assumed to be very large (> 500 K) and data with $T > \Theta$ are not available. In Table III we have listed the values of a and Θ of the *Cu*: Fe and *Au*: V systems in order to find a possible universal trend. The compilation shows that the values of a still differ considerably in the same system if different methods are used for their determination. In view of the scatter of the data it seems too early to draw any conclusions.

There is an alternate way to interpret the Mössbauer data[26] which yields somewhat different results in detail, but which fortunately does not change the general conclusions.

Kitchens and Taylor[26] use the equation (in the notation of the present paper)

$$H_{\rm hf} = (H_{\rm sat}/\mu)\, B_S\, [\mu H_0/k(T+\Theta)], \qquad (4a)$$

where B_S is the Brillouin function for spin S to fit hyperfine data. Using the data of Refs. 13 and 14 they obtain (using $g=2$) $\Theta = 26 \pm 1$ K, $\mu = (5.3 \pm 0.7)\mu_B$ and $H_{\rm sat} = -82 \pm 8$ kG, where the last two numbers are in disagreement with the present analysis. It should also be stressed that this value for μ does not agree with the one obtained from the macroscopic susceptibility data. We can only guess the reason for this discrepancy. First there is no theoretical argument for using relation (4a) over a large temperature and field range. Only in the limit of $T \gg \Theta$ and $H_0\mu_B/kT < 1$ does this expression coincide with the local magnetization, as demonstrated in recent theoretical calculations of Götze and Schlottmann.[3] Secondly, in contrast to other systems the *Cu*: Fe system does not allow, with presently available external fields, an unambiguous determination of $H^d_{\rm sat}$, because saturation has not

TABLE III. Values of a and Θ from the relation $\chi(T)/\chi(T=0) = 1 - a(T/\Theta)^2$ for $T < \frac{1}{5}\Theta$, for *Cu*: Fe and *Au*: V.

	Θ(K)	a	Method
Cu: Fe	28	2.9	Mössbauer experiments (< 10 ppm) Present results
Cu: Fe	29	15	Specific-heat data (81 ppm), Ref. 25 ($T < \frac{1}{15}\Theta$)
Au: V	300	1.2	NMR experiments (0.3%), Ref. 23
Au: V	300	2.8	Bulk magnetization (0.3%), Ref. 12
Au: V	300	4.1	Bulk magnetization (0.15%), Ref. 22

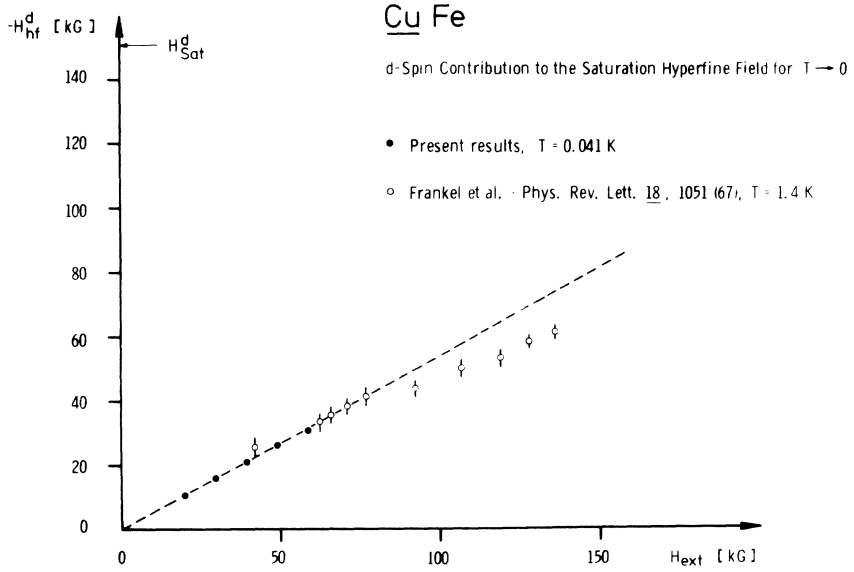

FIG. 7. d-spin saturation hyperfine field of ^{57}Fe in Cu from Mössbauer experiments as a function of the external field H_{ext} for $H_{ext}/T \to \infty$.

been ottained in any of the published data. This is best seen in Fig. 7, which shows the d-spin contribution to the hyperfine field for the lowest temperatures as function of the external field. In order to avoid possible complications due to the Kondo effect it seems therefore attractive to obtain the parameters for small values of the argument of the Brillouin function (large T). This yields

$$H_{hf} = H_{sat}\left(\frac{S+1}{S}\right)\left(\frac{\mu H_{ext}}{3k(T+\Theta)}\right) \qquad (4b)$$

and essentially allows the determination of the product $H_{sat}\mu$. This is 435 kG μ_B in the analysis of Kitchens and Taylor[26] as compared to 415 kG μ_B in the present analysis; this indicates that much of the above realized discrepancy may be due to the difficulty of separating H_{sat} and μ in the analysis of Ref. 25, whereas the remainder is certainly produced by the neglect of the temperature independent contribution to H_{hf} and slightly different experimental results.

ACKNOWLEDGMENTS

This work was supported by the Bundesministerium für Wissenschaft und Technologie.

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