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Magnetic Correlations in Spin Glasses above the Freezing Temperature investigated by High Field Mössbauer Spectroscopy*

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Abstract
The strong dynamics of magnetic correlations are observed by high field $^{57}$Fe Mössbauer investigations for the spin glasses AuFe and Y(Fe, Al)$_2$ in the temperature interval between the freezing temperature $T_f$ and approximately 7 to 10$T_f$. All recorded spectra can be analysed with a model which takes into account these dynamics by allowing the formation of correlated states after a stochastically varying time $\tau_{off}$ and their decay after a time $\tau_{on}$, restricting the number of subspectra to the different number of Fe atoms in the first neighbour shell. Whereas for the different Fe environments, in addition to centre shift and quadrupole splitting, different hyperfine fields of the two stochastically formed states can always be resolved, the same set of $\tau_{on}$ and $\tau_{off}$ values was obtained for all subspectra above approximately 4$T_f$. The external field hinders the decay of the correlated regions. The temperature dependence of $\tau_{on}$ scales with $T_f$ and exhibits a power law with exponents of $-2$ for the Fe-rich and $-1$ for the Fe-poor compounds.

1. Introduction

A spin glass can be characterised as a sample which contains atoms with permanent magnetic moments of such a concentration that randomness is conserved and long range magnetic correlations are avoided. If this sample is cooled from high temperatures $T$, where it is paramagnetic, into the temperature interval ranging from the freezing temperature $T_f$ up to temperatures of several times $T_f$, many of these freely rotating and randomly positioned spins build themselves gradually into correlated regions. The dynamical behaviour of these regions or magnetic clusters with changing temperature and/or external fields can be investigated by different experimental techniques such as ESR, NMR, $\mu$SR, neutron spin echo and neutron scattering, as well as Mössbauer spectroscopy, each having its own typical measuring time window (Murani 1978, 1981; Morgownik and Mydosh 1981; Mezei 1983; Uemura et al. 1985; Dattagupta 1989; Mydosh 1993).

In Mössbauer spectroscopy the nucleus represents an extremely local probe for changes of the charge and spin density around the atom and offers thus the possibility of getting information about individual spatial spin configurations.

In the above-mentioned temperature interval the dynamics of these correlated regions can be slowed down to times observable by $^{57}$Fe Mössbauer spectroscopy by applying external fields $B_x$. With fields of 10 to 15 T one enters for iron containing spin glasses the time window of $10^{-9}$ to $10^{-7}$ s which is just in between the one typical for neutron and $\mu$SR experiments (Dattagupta 1989). A knowledge of the dynamics of the different environments may help to gain an understanding for the precursors of the freezing process.

In the present paper we focus on two typical spin glasses: (i) $\text{Au}_{1-x}\text{Fe}_x$ where Fe is embedded in a diamagnetic host and (ii) $Y(\text{Fe}_x\text{Al}_{1-x})_2$ where Fe is substituted in a Pauli paramagnetic matrix. With some care chemical clustering of Fe in an amount resolvable by a Mössbauer transmission experiment can be avoided in both series. The freezing temperatures for all samples are below 50 K (Fig. 1). Since for experimental reasons the measuring temperature is limited to 295 K these samples provide us with the possibility of studying the dynamics in a wide temperature range and at quite different Fe concentrations.

2. Experimental Details

From the cubic Laves phases $Y(\text{Fe}_x\text{Al}_{1-x})_2$ (MgCu$_2$ structure type) samples with $x = 0.25, 0.40, 0.65$ and $0.75$ were prepared by induction melting in a water cooled copper boat under argon atmosphere, followed by a homogenisation at 700°C in evacuated quartz tubes. These are the same samples which were extensively studied in earlier investigations by means of magnetic and X-ray measurements (Reissner et al. 1984). In this structure type the Y atoms form two fcc lattices which are shifted by one quarter along the body diagonal. The
Fe atoms are arranged in top sharing tetrahedra. The Fe substitutes only for Al. Thus every Fe atom has six nearest neighbour sites which, depending on concentration, can be occupied either by Fe or Al.

\( \text{Au}_1 \times \text{Fe}_x \) samples with Fe concentrations of \( x = 0 \cdot 05, 0 \cdot 08 \) and \( 0 \cdot 15 \) were prepared from metallic \( \text{Au} \) and \( {}^{57}\text{Fe} \) (purity 6N and 3N respectively) using an electron gun and afterwards cold-rolled to foils of thickness of 3 \( \mu \text{m} \) (Yoshida et al. 1989) and 8–10 \( \mu \text{m} \) (Campbell 1996), again annealed and quenched. The alloys exhibit fcc structure. A strong indication that the formation of chemical clusters of Fe was avoided follows from the analysis of spectra recorded at room temperature without external field, because both the number and the intensity ratio of the subspectra needed for a reasonable fit are in complete agreement with the ones following from a binomial distribution. Long range magnetic order which is extremely inhomogeneous is reported to be present for \( x \) larger than approximately \( 0 \cdot 16 \) (e.g. Sarkissian 1981).

Because of the different time windows of the measurement techniques, the freezing temperature \( T_a \) determined from a diminishing of the magnetic hyperfine splitting of the \( {}^{57}\text{Fe} \) Mössbauer spectra recorded without an external field is always slightly higher than the temperature \( T_f \) obtained from magnetic measurements in low dc fields (see Fig. 1). For the \( \text{AuFe} \) samples the values are in complete agreement with the ones collected by Sarkissian (1981).

The \( {}^{57}\text{Fe} \) Mössbauer measurements were performed in the temperature range 4.2 to 275 K in external fields up to 13.5 T (a maximum field of 15 T can be achieved). The direction of \( B_a \) is parallel to the \( \gamma \)-ray direction. For the source (\( {}^{57}\text{CoRh} \)) a field compensated area \( (B_a < 0.1 \text{ T}) \) is available. The linewidths obtained for an \( \alpha \)-Fe absorber were 0.24 mm/s. The temperature of the source was kept between 4.2 and 40 K, depending on the absorber temperature, which was measured by a carbon glass resistor and controlled by a field-independent SrTi sensor. A temperature stability of ±0.1 K was achieved over the measuring times, which were between two and five days apart, because of the large distance of 50 cm between source and proportional counter. A second source was mounted at the rear of the drive, which together with a separate absorber and counter equipment allows the simultaneous calibration of the velocity at room temperature.

Applying an external field at temperatures above approximately seven times \( T_f \) leads to Mössbauer spectra which are split by an effective magnetic hyperfine field \( B_{hf} = B_a - B_{ind} \). Here \( B_{ind} \) is the field due to the paramagnetic moments, which increases with \( B_a \) and decreasing \( T \). The contributions of the \( \Delta m = 0 \) transitions in the spectra are suppressed, thus \( B_{hf} \) is oriented parallel to \( B_a \). The shape of the spectra can be reproduced by superposition of several subspectra. The number and relative intensity ratios of these subspectra are determined by the different number of Fe atoms in the nearest neighbour shell (Püsing et al. 1989). The intensity ratios follow from the binomial distribution function. Small differences in \( B_{hf} \), electric quadrupole splitting and centre shift appeared, the latter two in complete agreement with the analyses of the measurements in zero field, which are also performed with the identical number and intensity ratio of subspectra (Reissner et al. 1984). These spectra are characteristic of samples exhibiting paramagnetic behaviour within the time window of the experiments.

At temperatures between \( T_f \) and approximately 7–10\( T_f \), however, the response to the external field is completely different (see Fig. 2). Most Mössbauer results
Fig. 2. The $^{57}$Fe Mössbauer spectra of Au$_{0.92}$Fe$_{0.08}$ measured without and with an external field of 13.5 T at 50 K. The four subspectra used for the analysis for Fe with a different number of Fe nearest neighbours are also shown.

reported in the literature for samples of similar concentrations were analysed by means of static hyperfine field distributions in the limit of fast relaxation (Meyer and Hartmann-Boutron 1990; Furukawa et al. 1990) with a large number of subspectra. The overall shape of the recorded spectrum, however, is characterised by flat shoulders at large positive and negative velocities, strongly indicating the presence of fluctuating hyperfine fields within the time window of the experiment. A model, which takes into account these dynamics in proposing that the magnetic correlated regions form and decay stochastically, allows a fit to the spectra more consistently with the ones recorded without external fields. Since now the same number of subspectra at all temperatures is used, information about the dynamics of a distinct environment can be achieved (Posinger et al. 1991b, 1992a, 1992b).

3. Results and Discussion

The main results obtained from the in-field measurements of the 75% sample of the Y(Fe, Al)$_2$ series fitted with hyperfine field distributions can be summarised
as follows: The distribution extends over both sides of $B_a$. The spectra are fully polarised ($\Delta m = 0$ transitions suppressed). Thus, hyperfine fields both larger and smaller than $B_a$ must be present. This is only possible if some of the internal fields acting on the $^{57}$Fe nucleus are parallel and some are antiparallel to the applied field. The Fe moments are in that case also either antiparallel or parallel oriented to the applied field. It was shown for this Fe concentration that only the core contribution to the hyperfine field is essential (Pössinger et al. 1993a). For the parallel component one ends up with fields and thus Fe moments which are larger than those of the magnetically long range ordered boundary compound YFe$_2$, which is not physically reasonable.

The existence of short range correlations up to temperatures several times $T_f$ has been proved by a number of experiments (Murani 1978, 1981; Morgownik and Mydosh 1981; Mezei 1983; Uemura et al. 1985; Mydosh 1993). The growth in size with decreasing temperature, as well as the rotation in external fields, of the net magnetisation of these correlated regions is used to explain the experiments (Mydosh 1993). What has been neglected in this description and what is strongly supported by the overall shape of the measured in-field Mössbauer spectra is the inclusion of a dynamical behaviour of these correlations, in such a way that they form and decay in the course of time leading to the following model for the magnetic exchange interaction above $T_f$ (Pössinger et al. 1991b, 1993b; Pössinger 1992): At high temperatures the sample is paramagnetic. With decreasing temperature regions start to form where Fe moments are correlated for a certain time. In the course of time these correlations are not stable, they decay and form again, a process which continues stochastically. In an external field the Mössbauer nucleus is therefore during an average time interval $\tau_{on}$ exposed to the field resulting from the vectorial sum of the applied field and the field caused by the correlated spins (see Fig. 3), while during the following time interval $\tau_{off}$ this Fe nucleus does not take part in such a correlation. Similar to a nucleus in the paramagnetic state it is during the latter time interval exposed to the field resulting from the sum of $B_a$ and $B_{ind}$. Simplifying, one may say that the external field stabilises the correlations in a way that a stable magnetisation results for a time $\tau_{on}$, which produces the field $B_{cl}$. Further, these time intervals $\tau_{on}$, during which the correlations exist, are interrupted by periods $\tau_{off}$, during which the correlations have disappeared so that the Mössbauer nuclei remain in the uncorrelated environment.

![Fig. 3. Schematic description of the model and the corresponding fitting parameters.](image-url)
The switching between the two situations is assumed to occur instantaneously in a kind of a stochastic process with probabilities \( w(\text{on} \to \text{off}) = 1/\tau_{\text{on}} \) and \( w(\text{off} \to \text{on}) = 1/\tau_{\text{off}} \). The dynamics observable in the Mössbauer spectra result from the fact that the time \( \tau \) derived from \( 1/\tau = 1/\tau_{\text{on}} + 1/\tau_{\text{off}} \) is under the present conditions found to be of the order of the Mössbauer time window given by the Larmor period of the absorbing Fe nucleus in the effective magnetic field. The ratio of the two times \( a_\tau = \tau_{\text{on}}/\tau_{\text{off}} \) enters in addition to \( \tau \) as the second dynamical parameter in the fitting procedure.

The shape of the spectra can be calculated within the stochastic theory of Clauser and Blume (Blume 1965, 1968; Blume and Tjon 1968; Clauser 1971; Clauser and Blume 1971; Winkler et al. 1988). The Hamiltonian in terms of which the nuclear Zeeman and the electrostatic hyperfine interactions can be described is, for fields acting at the nucleus which are collinear with the \( \gamma \)-ray direction, of the form

\[
H = -g_N\mu_N [B_a - B_{\text{ind}}(1 - f(t))] - B_{\text{cl}}f(t)I_z
\]

\[
+ \frac{eQV_{zz}}{4I(2I - 1)} \{ \frac{1}{2}(3\cos^2 \beta - 1)(3I_z^2 - I^2) \\
+ \frac{3}{2}\sin2\beta[(I_zI_x + I_xI_z)\cos\Phi + (I_zI_y + I_yI_z)\sin\Phi] \\
+ \frac{3}{2}\sin^2 \beta[(I_x^2 - I_y^2)\cos2\Phi + (I_xI_y + I_yI_x)\sin2\Phi] \}
\]

where \( \beta \) and \( \Phi \) are the angles of the largest contribution of the electric field gradient tensor \( V_{zz} \) with respect to the laboratory frame and \( f(t) \) denotes a random variable taking the values 0 or 1. Restricting the model to the two states—correlated and paramagnetic—leads to a matrix of size 16×16 only. Close to \( T_f \) it is necessary to admit an angle \( \vartheta \) between \( B_{\text{cl}} \) and \( B_a \). For the present results it was assumed that \( \vartheta \) remains unchanged if the correlation is re-established.

In fitting the spectra different values for \( B_{\text{ind}} \) and \( B_{\text{cl}} \) for different environments were allowed under the restriction that both increase with increasing number of Fe neighbours. Following the zero field results the quadrupole splitting does not depend on temperature and the centre shift changes with temperature due to the quadratic Doppler effect. These changes are assumed to be the same for all configurations, which means that the Debye temperature does not depend on the local environment. This assumption seems to be reasonable for a metal. For the linewidth the same value as measured for the \( \alpha \)-Fe foil was used. The asymmetry parameter of the electric field gradient was set to zero.

All measured spectra could be fitted reasonably well within this model. Typical examples are shown in Figs 4 and 5. It must be stressed once again that the number of subspectra remains the same for the zero field and the in-field measurements. Because of the random distribution of the Fe atoms the relative intensity ratios for the subspectra are calculated from the binomial distribution and are not free fitting parameters (see e.g. Fig. 2). Thus the discrimination between individual Fe environments remains.
Fig. 4. The $^{57}$Fe Mössbauer spectra of Y(Fe$_{0.75}$Al$_{0.25}$)$_2$ recorded in different external fields at 70 K (left) and 200 K (right). The curves give the fit according to the model described.

Fig. 5. The $^{57}$Fe Mössbauer spectra of Au$_{1-x}$Fe$_x$ for $x = 0.05$ (left) and $x = 0.08$ (right) recorded in different external fields at 100 K. The curves give the fit according to the model described.
Fig. 6. Temperature dependence of the fields $B_{cl}$ acting during $\tau_{on}$ at Fe atoms with a certain number of nearest Fe neighbours for $Au_{1-x}Fe_x$ for $x = 0.05$ (left), $x = 0.08$ (middle) and $x = 0.15$ (right). The applied field was 13.5 T. The lines are guides to the eye.

Fig. 7. Dependence on $B_a/T$ of the fields $B_{ind}$ acting during $\tau_{off}$ at Fe atoms with a certain number of nearest Fe neighbours for $Au_{1-x}Fe_x$ for $x = 0.05$ (left), $x = 0.08$ (middle) and $x = 0.15$ (right). The lines are guides to the eye.
During the time $\tau_{on}$ the Mössbauer atom is part of a correlated region where the nucleus is exposed to a hyperfine field $B_{cl}$. For temperatures higher than approximately twice $T_f$, these fields are oriented antiparallel to $B_a$. Near $T_f$, however, even at 13.5 T, complete alignment was not always achieved. For both the AuFe and the Y(Fe, Al)$_2$ series $B_{cl}$ decreases with temperature, and is only mildly dependent on $x$ for a given environment (see Fig. 6). In Fig. 6 the symbols end at those temperatures for which the times $\tau_{on}$ and $\tau_{off}$ become too short to be determined within the Mössbauer time window.

During $\tau_{off}$ the Fe atom does not take part in any correlation and must therefore exhibit paramagnetic behaviour. The field $B_{ind}$ acting on the nucleus during this time is only caused by the response of the probe atoms own moment on $B_a$. For a paramagnetic state one would thus expect a Brillouin-like behaviour, which is really found for all different Fe environments (e.g. $B_{ind}$ versus $B_a/T$ for the three AuFe samples in Fig. 7). The induced fields increase with the number of Fe neighbours and the value obtained for Fe completely surrounded by Au is in good agreement with the one observed from investigations of other dilute AuFe alloys, which do not take into account any dynamics (Steiner et al. 1974). This result supports strongly the proposed model and the fact that, within this model, information about the magnetic state of a distinct local environment is available.

Further support can be obtained from a comparison with bulk magnetic measurements. The time dependence in the dynamical data can be averaged by calculating a field $B_n$ defined by

$$B_n = \frac{B_{cl} \tau_{on} \cos \theta + B_{ind} \tau_{off}}{\tau_{on} + \tau_{off}}.$$ 

![Fig. 8. Field dependence of magnetisation $\sigma$ (open symbols) and $B_n$ (full symbols) for Y(Fe$_{0.75}$Al$_{0.25}$)$_2$ at 50 K (squares), 160 K (circles) and 240 K (triangles). For the definition of $B_n$ see above.](image-url)
Fig. 9. Temperature dependence of $\tau_{\text{off}}$ (left) and $\tau_{\text{on}}$ (right) averaged over the different Fe environments for $\text{Au}_{0.92}\text{Fe}_{0.08}$ at different external fields.

Fig. 10. Temperature dependence of $\tau_{\text{off}}$ (left) and $\tau_{\text{on}}$ (right) averaged over the different Fe environments for $\text{Y(Fe}_{0.75}\text{Al}_{0.25})_2$ at different external fields.
Fig. 11. Comparison of the temperature dependence of $\tau_{\text{off}}$ for some Fe-poor (left) and Fe-rich (right) samples.

Fig. 12. Mean lifetime $\tau_{\text{on}}$ of the correlated states at $13.5 \, T$ as a function of the reduced temperature for the series Y(Fe$_x$Al$_{1-x}$)$_2$ and Au$_{1-x}$Fe$_x$. 

\( Y(\text{Fe}_x\text{Al}_{1-x})_2 \)

\[ \nabla \quad 0.75 \]

\[ \blacksquare \quad 0.65 \]

\[ \square \quad 0.40 \]

\[ \blacklozenge \quad 0.25 \]

\( \text{Au}_{1-x}\text{Fe}_x \)

\[ \blacktriangle \quad 0.15 \]

\[ \circ \quad 0.08 \]

\[ \blacklozenge \quad 0.05 \]
This field acts on the $^{57}$Fe nucleus and must for that reason be comparable with the macroscopically measured magnetisation. Since in Y(Fe$_{0.75}$Al$_{0.25}$)$_2$ the core contribution is the dominant part of the hyperfine field (Pösinger et al. 1993a), $B_n$ is in addition directly proportional to the bulk magnetisation (see Fig. 8). In the comparison there is only one free parameter left (the hyperfine coupling constant), which turns out to be 11 T/$\mu_B$ for all temperatures, again in good agreement with the values determined from standard Mössbauer experiments.

The analysis of the spectra recorded at temperatures above approximately 4$T_f$ was possible with only one set of $\tau_{on}$ and $\tau_{off}$ for all different environments. This might be an indication that for these temperatures the probable distribution of correlation times (Mydosh 1993; Murani 1981; Uemura et al. 1985; Campbell et al. 1994) gets very narrow. At lower temperatures different values must be used, and both $\tau_{on}$ and $\tau_{off}$ increase with an increasing number of Fe atoms in the first neighbour shell. The temperature dependence of the average over the different surroundings of these times is quite similar for all field values (see Figs 9 and 10). The increase of $\tau$ with $B_n$ shows that the external field stabilises already existing correlations. The values for $\tau$, which are a measure for the transition probability from the paramagnetic to the correlated state, exhibit for the samples with low Fe content the expected increase with temperature. For Fe-rich samples of both series, however, a decrease with $T$ is obtained (see Fig. 11). Nevertheless, for both high and low Fe concentration the ratio $\tau_{off}/\tau_{on}$ increases with increasing temperature. Since the reciprocal values of these times are correlated with the probability of formation and/or decay of a correlated region this implies, following general scaling arguments (e.g. Ogielsky 1985; Rieger 1995), that larger regions are integrated into the dynamics.

Within the present model $\tau_{on}$ can be assumed to be proportional to the spin auto-correlation function. As a function of the reduced temperature $t = T/T_f$ power laws are obtained for all samples with exponents $-2$ for the Fe-rich and $-1$ for the Fe-poor samples (see Fig. 12). In addition, for compounds with higher Fe content the $\tau_{on}$ values of both series coincide, whereas for those with small Fe content only the exponent is the same. At the present state of our experiments it is not conclusive whether this change in exponent is connected with a change in the dominant magnetic exchange interaction. Investigations on AuFe samples with 10% and 12% Fe are in progress. Preliminary results for the spin glasses formed in the CrFe and NiFeMn systems fit completely in the behaviour sketched above and also show the same exponents for the power law of $\tau_{on}$ ($T$).

4. Summary

The results of our investigations on the magnetic behaviour above the freezing temperature of the spin glasses Au$_{1-x}$Fe$_x$ and Y(Fe$_x$Al$_{1-x}$)$_2$ can be summarised as follows:

- Magnetic correlations exhibiting strong dynamics are present in all compounds above $T_f$ and can be investigated by means of high field Mössbauer spectroscopy up to temperatures of approximately 7 to 10$T_f$.

- The proposed model of a stochastic formation of magnetic correlations which decay after a time $\tau_{on}$ and are formed again after a time $\tau_{off}$ is able to describe the recorded Mössbauer spectra of Fe substituted in the diamagnetic host Au, as well as in the Pauli paramagnetic host YAl$_2$ over a broad range
of Fe concentrations.

- The dynamics of the correlated regions can be resolved for the different Fe environments and seem to be dominated by nearest neighbour exchange interactions.
- The applied field hinders the decay of these correlations.
- Above approximately 4$T_f$ only one set of $\tau_{on}$ and $\tau_{off}$ values for the different Fe environments was obtained, indicating a narrowing of the probable distribution of correlation times.
- The dependence of $\tau_{on}$ (averaged over the different Fe environments) on the reduced temperature $T/T_f$ exhibits a power law with an exponent which appears to be typical for Fe-rich and Fe-poor samples.

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