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A Mössbauer spectroscopic investigation of the dynamics of magnetic correlations in the spin glasses Au(Fe) and $Y(Fe, Al)_2$ above T_f

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Abstract. Transmission ^{57}Fe Mössbauer spectra of the typical spin glasses $Y(Fe_xAl_{1-x})_2$ ($x = 0.75, 0.65, 0.40, 0.25$) and $Au_{1-x}Fe_x$ ($x = 0.15, 0.05$) were taken from 4.2 K up to room temperature in applied fields (B_a) up to 15 T. To account for the correlations which appear at temperatures $T \lesssim 7$ times the freezing temperature (T_f) a model is employed according to which magnetic correlations are formed and decay in the course of time. The resulting field values fit to those at higher temperatures and to the zero-field spectra at 4.2 K. The mean relaxation times depend linearly on $B_a^{1/2}/T^{3/2}$ and scale with T_f. The mean lifetime of the correlations scales with T/T_f and increases with increasing B_a and decreasing temperature, whereas the mean time during which the Fe atoms are uncorrelated is only mildly dependent on B_a, which indicates that the applied field does not favour the formation of correlations but that it stabilizes the correlations if their magnetic moment is oriented parallel to B_a. Three to five Fe atoms are included in the correlated regions.

1. Introduction

Above the freezing temperature (T_f) of spin glasses up to approximately five to seven times T_f exists a region in the magnetic phase diagram where the behaviour deviates from that characteristic for paramagnets. The magnetization curves are non-linear in this temperature range and Curie–Weiss behaviour is only found at higher temperatures [1]. Different experimental techniques like ESR, NMR, muon precession, neutron spin echo experiments and neutron scattering all point to a gradual formation of correlations in the spin system with decreasing temperature and to the existence of dynamical processes [2–6].

^{57}Fe Mössbauer spectra without applied field are magnetically unsplit above a temperature which is slightly higher than T_f. Applying an external field B_a at high temperatures ($T > 7T_f$) leads to spectra which are split by an effective magnetic hyperfine field $B_{hf} = B_a - B_{ind}$, with B_{ind} being a small induced field increasing with increasing B_a and decreasing temperature (T). B_{hf} is oriented parallel to B_a. The spectra consist of subspectra with small differences in B_{hf}, electric quadrupole splitting ($eQV_{zz}/2$) and centre shift originating from the different number of Fe atoms in the nearest neighbour shell. At lower temperatures ($T_f < T \lesssim 7T_f$) the shape of the spectra changes. Analyses within the limit of fast relaxation would lead to broad distributions of hyperfine fields with field values which are rather implausible [7]. In contrast, within a model of stochastically forming and decaying magnetic correlations the spectra can be fitted more consistently with the same number of subspectra at all temperatures and information about the dynamics can be

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achieved [8–10]. It is the aim of this paper to present the results obtained within this model for the dynamics of the formation of the magnetic order in the two series $Au_{1-x}Fe_x$ and $Y(Fe_xAl_{1-x})_2$ and to give an estimation of the size of the correlated regions.

2. Experimental details

Samples with Fe concentrations of $x = 0.05$ and 0.15 for $Au_{1-x}Fe_x$ were prepared [11] from metallic Au and ^{57}Fe (purity 6N and 3N, respectively) using an electron gun and cold-rolled to foils of thickness of 3 μm. Four samples with $x = 0.25$, 0.40, 0.64 and 0.75 were prepared from the series $Y(Fe_xAl_{1-x})_2$ by induction melting of the metals (purity 3N for Y and higher than 4N for Fe and Al) under purified argon atmosphere, followed by homogenization at 700 °C in an evacuated quartz tube [1]. The AuFe alloys are of the FCC structure type and the Laves phase $Y(Fe,Al)_2$ crystallizes in the cubic $MgCu_2$ (C15) structure type except in a small region around $x = 0.55$ which was avoided in the present investigation. In both series the Fe atoms occupy the respective lattice sites randomly. All samples were checked to be single phased by x-ray diffraction measurements. A strong indication that chemical clusters of Fe are avoided in the AuFe samples follows from the analyses of the quadrupole-split Mössbauer spectra recorded without external field at room temperature. If Au is substituted statistically by Fe, both the number and intensity ratio of the subspectra are given by a binomial distribution. At $x = 0.05$ this leads to three subspectra in $Au_{1-x}Fe_x$ with ^{57}Fe surrounded by zero, one and two Fe nearest neighbours. The quadrupole splitting for Fe surrounded only by Au is almost zero because of the symmetry of the structure. One Fe neighbour disturbs the symmetry and leads to higher values of $eQV_{zz}/2$. A higher number of Fe neighbours results in somewhat lower values of $eQV_{zz}/2$. The measured values are in complete agreement with these expectations (e.g. figure 1).

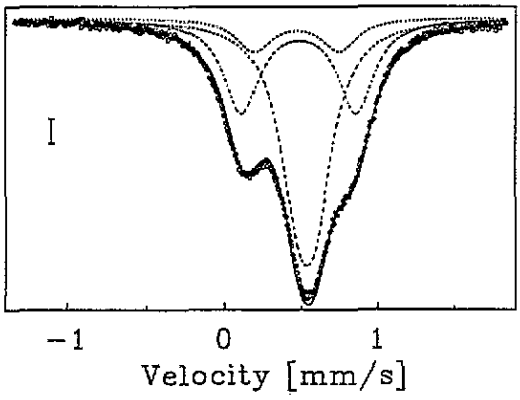

Figure 1. ^{57}Fe Mössbauer spectrum of $Au_{0.95}Fe_{0.05}$ at room temperature without external field. The broken lines give the calculated subspectra (– – – 0, — · — 1, · · · · · · 2 or 3 nearest neighbours Fe). The bar represents 1% reduction in count rate.

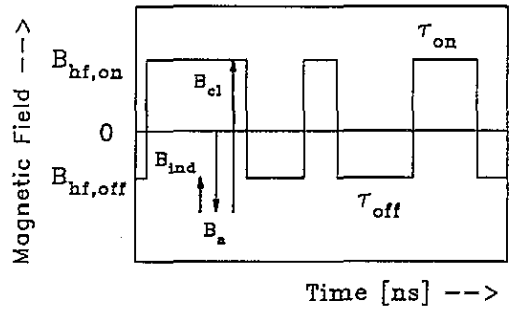

Figure 2. Schematic representation of the model parameters.

The freezing temperatures of the samples are 45 and 27 K for $x = 0.15$ and 0.05 in AuFe [12] and 39 K (26, 9.5 and ~ 4 K) for $x = 0.75$ (0.65, 0.40, 0.25) in $Y(Fe_xAl_{1-x})_2$.

Long range magnetic order is present in **Au**Fe at concentrations above $\sim$ 16 at.% Fe and at $x \geqslant 0.78$ in $Y(Fe_xAl_{1-x})_2$.

Spectra were recorded in transmission geometry between 4.2 K and room temperature in applied fields up to 15 T. The field direction was always parallel to the γ-direction. Details of the experimental set-up are described in [13]. Due to the long distance between the ^{57}**Co**Rh source and the counter, measuring times between two and five days were necessary. The temperature of the samples was kept constant with an error of < 0.25 K over the measuring time.

3. Description of the model

The presence of short range magnetic correlations in spin glasses up to temperatures of several times T_f is generally assumed e.g. [2]. The growth in size of these locally correlated regions with decreasing temperature, and rotation of the resulting magnetization of these spin clusters is used as explanation for the experimental results [2]. What has been neglected in this description is the possibility of a dynamical behaviour such that the correlations form and decay in the course of time. We think that our Mössbauer measurements in the temperature range below 7 T_f require an alternative description with inclusion of this type of dynamics. In zero field above T_f the dynamics of the magnetic correlations is too fast to be resolved within the time window of Mössbauer spectroscopy. In an applied field the mean lifetime of magnetic correlations with resulting effective magnetic moment close to the direction of B_a is increased by B_a. For an Fe atom which is a member of a correlated region the effective hyperfine field is the vector sum of B_a and B_{cl}. The field B_{cl} results from the magnetization of the correlation (figure 2) and its value is determined by the polarization of the electrons of the individual Fe probe atom which itself depends on the number of nearest Fe neighbours. After a mean lifetime τ_{on} the correlation decays and the Fe probe is exposed to the field $B_a - B_{ind}$. The field B_{ind} is oriented antiparallel to B_a and is caused by the Fe moment in the paramagnetic state. It takes a mean time τ_{off} before the Fe atom is again included in a correlated region.

The shape of the spectra is calculated within the stochastic theory of Clauser and Blume [14–19]. Restricting the model to two states (correlated and paramagnetic) leads to a relaxation matrix of size 16 × 16 only, which ensures short calculation times. Close to T_f it is necessary to admit an angle (θ) between the internal field and B_a in the correlated state. Generally it was assumed that this angle remains unchanged if the correlation is re-established, thereby keeping the size of the relaxation matrix constant.

In fitting the spectra the fractional contributions of various environments, i.e. nearest-neighbour Fe atoms, were taken according to the binomial distribution. Different values for the centre shift, eQV_{zz}, B_{ind} and B_{cl} for different environments were allowed whereby B_{ind} and B_{cl} were assumed to increase with increasing number of Fe neighbours. The possibility of having different sized correlated regions which may cause different dynamical parameters τ_{on} and τ_{off} was taken into account by allowing for two or more different values of the dynamical parameters [20]. In the following τ_{on} and τ_{off} refer to the resulting mean values.

For the line width Γ a value of 0.3 mm s^{-1} as measured for an α-Fe foil was used for all subspectra. The asymmetry parameter of the electric field gradient was set to zero. The parameters to be fitted were changed by hand to find the minimum in the χ^2-deviation by trial and error. The philosophy of the fitting was to keep the model as simple as possible and the number of parameters low. The remaining discrepancies (figure 1 and 3) may be

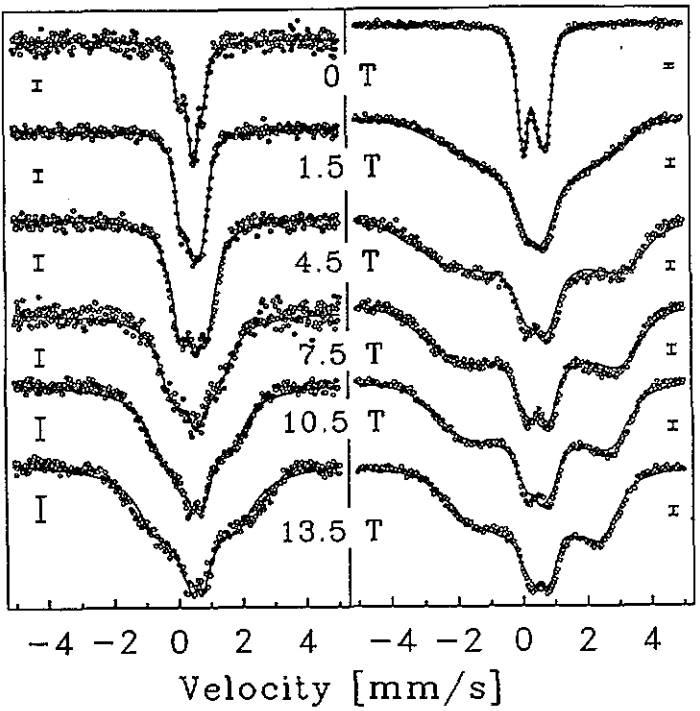

Figure 3. Measured (circles) and fitted (lines) ^{57}Fe Mössbauer spectra of $Au_{1-x}Fe_x$ at $T = 100$ K and different B_a. Left (right) side: $x = 0.05$ (0.15). The bars represent 1% reduction in count rate.

attributed to additional variances of the hyperfine field due to next-nearest-neighbour effects and the restriction that only one value for θ was used.

4. Results

In the whole temperature range between T_f and 300 K the zero-field spectra show only quadrupole splitting (figures 1 and 3). Application of an external field B_a leads to magnetic splitting of the spectra which increases with increasing B_a. Close to T_f even small external fields lead to large splittings (e.g. the spectrum of $Au_{0.85}Fe_{0.15}$ at $B_a = 1.5$ T and $T \sim 2T_f$, right-hand side of figure 3).

At high temperatures the vanishing of the second and fifth lines in the spectra and the values of B_{hf} indicate that B_{ind} is oriented antiparallel to B_a. The spectra can be analysed within the fast relaxation limit with a set of subspectra according to a binomial distribution. At lower temperatures ($< 7T_f$) the shape of the spectra is typical for the presence of dynamical effects: high absorption at low absolute values of the velocity, and broad shoulders at higher velocities (figures 4 and 5). Maintaining the analyses in the fast relaxation limit would lead to components in the spectrum with parallel alignment of B_{ind} with respect to B_a or to internal fields which are higher in $Y(Fe, Al)_2$ than in magnetically undiluted YFe_2.

The values of B_{ind} follow a Brillouin dependence on B_a/T but it was not possible to determine the saturation values as the uncertainties in the determination of B_{ind} increase with decreasing T.

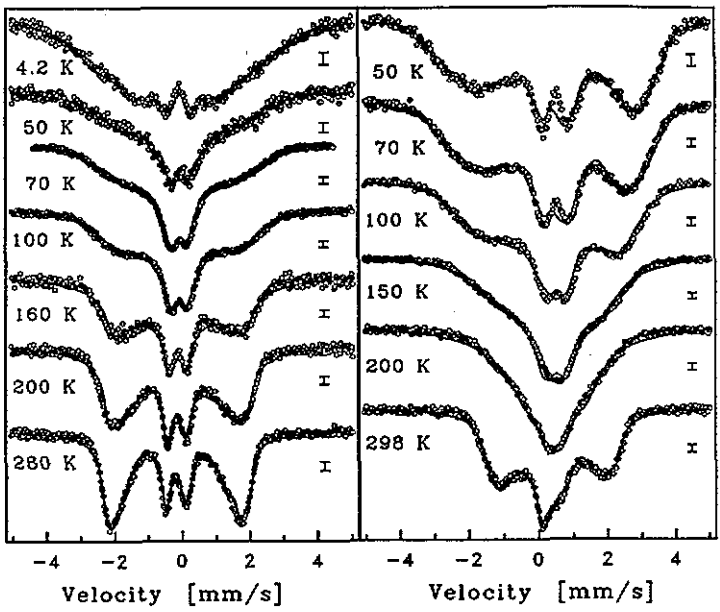

Figure 4. Measured (circles) and fitted (lines) ^{57}Fe Mössbauer spectra of $Y(Fe_{0.75}Al_{0.25})_2$ (left-hand side) and $Au_{0.85}Fe_{0.15}$ (right-hand side) at $B_a = 13.5$ T and different T. The bars represent 1% reduction in count rate.

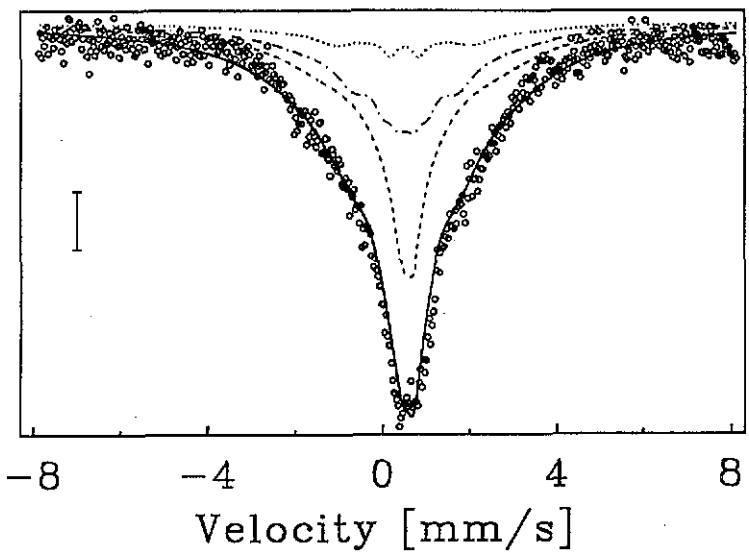

Figure 5. ^{57}Fe Mössbauer spectrum of $Au_{0.95}Fe_{0.05}$ at $T = 50$ K and $B_a = 10.5$ T. The broken lines give the calculated subspectra (– – – 0, — · — 1, ····· 2 or 3 nearest neighbours Fe). The bar represents 1% reduction in count rate.

The values of B_{cl} are nearly independent of B_a and decrease with increasing T. At T_f they are only slightly lower than the values obtained for B_{hf} at $T = 4.2$ K and $B_a = 0$. At

higher temperatures τ_{on} decreases and the shape of the spectra is insensitive to changes in the values of B_{cl} which makes it impossible to determine B_{cl} up to room temperature with satisfactory accuracy.

At temperatures $2T_f \lesssim T \lesssim 7T_f$ both B_{ind} and B_{cl} are oriented antiparallel to B_a whereas at temperatures below $2T_f$ the quality of the fits improves when deviations of B_{cl} from this direction are allowed. The value of the angle (θ) between B_a and B_{cl} increases with decreasing T and is between 40 and 50 degrees close to T_f even in high external fields, which is not too surprising as the application of an external field does not align the internal fields in spin glasses below T_f and the value of T_f strongly depends on the time window of the measuring method used for its determination.

The time τ_{off} which is defined as $1/w_{off\to on}$, where $w_{off\to on}$ is the transition probability from the paramagnetic state to the correlated state, is nearly independent of B_a (figure 6(a)). This indicates that B_a does not support the formation of the correlations. The increase of τ_{on} with increasing B_a (figure 6(b)) shows that B_a stabilizes existing correlations. Also the temperature dependence of τ_{off} is weaker than the one of τ_{on} (figure 6).

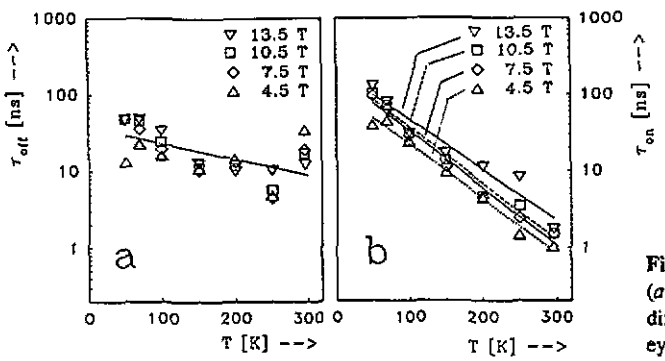

Figure 6. Temperature dependence of (a) τ_{off} and (b) τ_{on} for $Au_{0.85}Fe_{0.15}$ at different B_a. The lines are guides to the eyes.

The value $p = \tau_{on}/(\tau_{on} + \tau_{off})$ gives the mean fraction of time during which an ^{57}Fe probe is incorporated in a correlation. Since it is a statistical expression it also gives the mean fraction of Fe atoms which are situated in any correlated region at a given moment. p increases nearly linearly with decreasing T at high B_a ($\gtrsim 7.5$ T). At lower B_a it remains small down to approximately $2T_f$ and then increases more steeply. Close to T_f more than 70% of the Fe atoms take part in correlations in $Y(Fe_{0.75}Al_{0.25})_2$ and $Au_{0.85}Fe_{0.15}$. At lower Fe concentrations p is lower at the same T and B_a than at higher x.

The fact that no long-range order is present, even when a high percentage of the Fe atoms is correlated to other Fe atoms, indicates that there might exist some kind of frustration typical of spin glasses.

The ratio of the value $(B_{cl}\cos(\theta)\tau_{on} + B_{ind}\tau_{off})/(\tau_{on} + \tau_{off})$ to the bulk magnetization gives a value of 11 T/μ_B for all temperatures in $Y(Fe_{0.75}Al_{0.25})_2$. This linear relation supports the used model, as is to be expected, since at high Fe concentrations in $Y(Fe, Al)_2$ the contribution of the valence electrons to B_{ind} is small and thus the measured hyperfine field represents the core contribution which is directly related to the magnetic moment.

Independently of the applied field for both series, the values of τ_{on} as a function of the reduced temperature $t = T/T_f$ lie on the same straight line in a double logarithmic representation. This applies to all samples with the exception of those with the lowest Fe concentration as for example is shown for $B_a = 13.5$ T in figure 7. The lines correspond to $\tau_{on} \propto t^{-2}$ (higher Fe concentrations) and $\tau_{on} \propto t^{-1}$ (lowest Fe concentrations).

The relaxation time τ given by the equation $1/\tau = 1/\tau_{on} + 1/\tau_{off}$ shows a common, approximately linear, variation with $B_a^{1/2}/t^{3/2}$ for all samples investigated, at all measuring temperatures and for all applied fields (figure 8). Again, in this representation the slope for the samples with the lowest Fe concentrations (5% in AuFe and 25% in $Y(Fe,Al)_2$), is different. The dependencies found for τ_{on} and τ seem to be more than just a coincidence, as they hold for a wide variety of temperatures and fields. However, their significance must still be sought in terms of a theory of spin glasses which also takes into account dynamical effects above T_f.

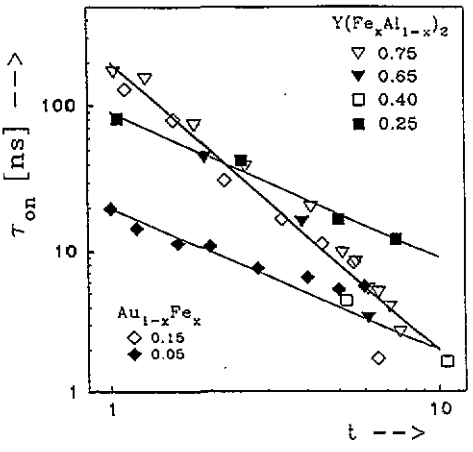

Figure 7. Dependence of τ_{on} on $t = T/T_f$ at $B_a = 13.5$ T for all samples of both series. The lines are explained in the text.

Figure 8. Double logarithmic representation of the mean relaxation time in $Au_{1-x}Fe_x$ ($x = 0.05$ ◆, 0.15 ◇) and $Y(Fe_xAl_{1-x})_2$ ($x = 0.25$ ■, 0.40 □, 0.65 ▼, 0.75 ▽).

All given values of the dynamic parameters τ_{on}, τ_{off}, τ and τ_{on}/τ_{off} are mean values over the distributions of these values present in the samples. It is not possible to give values for the lower and higher cut-offs of these distributions since at both boundaries of the time window the shape of the spectra is rather insensitive to changes of these parameters.

5. Discussion

The model of forming and decaying magnetic correlations used is suitable to explain the recorded spectra with reasonable values of the magnetic hyperfine fields. The decay of the correlations might possibly be described as indicated in figure 9. Without an external field the energy of a correlated Fe atom would be lower than that of the atom in the paramagnetic state due to the exchange interactions with its neighbours, but the entropy for a number of uncorrelated Fe atoms would be much higher than for the same number of correlated atoms because there are more possible arrangements for the uncorrelated ensemble. If the difference in the energy is not too large the entropy can no longer be neglected. In an applied field the probability of states being occupied such that the Fe moment is parallel or almost parallel to B_a increases, but all magnetic sub-states are allowed in paramagnetic atoms and transitions between different spin directions take place so fast that only a resulting B_{ind} is visible in the Mössbauer spectra. The energy of the resulting state is shifted to lower

values by $B_a\langle\mu_{Fe}\rangle$ where $\langle\mu_{Fe}\rangle$ is the thermal average of the Fe magnetic moment of an uncorrelated Fe atom. For correlated Fe atoms there will be an axial anisotropy inherent in the exchange interaction which permits only parallel or antiparallel orientation of μ_{cl} in analogy to superparamagnetic systems [21]. The state with the direction of the resulting moment μ_{cl} parallel to B_a is shifted by $-\mu_{cl}B_a$ to lower values, and for antiparallel alignment by $\mu_{cl}B_a$ to higher values, with μ_{cl} the effective magnetic moment of a correlated region. If the magnetic moment of a correlated region changes its direction from close to parallel to close to antiparallel with respect to B_a, the high entropy of the paramagnetic state would favour its occupation even if the energy of the correlated state was comparable to that of the paramagnetic state (figure 9). Thus within this picture a decay of the correlation results.

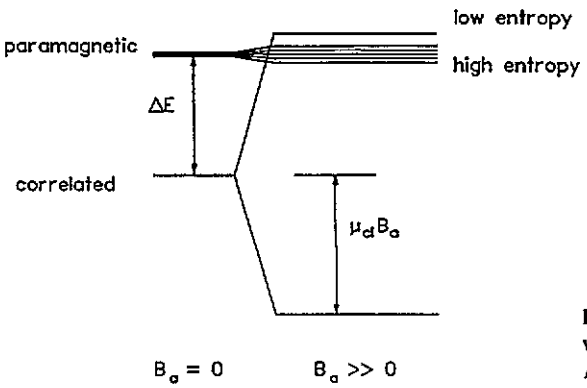

Figure 9. Energy level scheme of the two states which are allowed in the model with and without B_a.

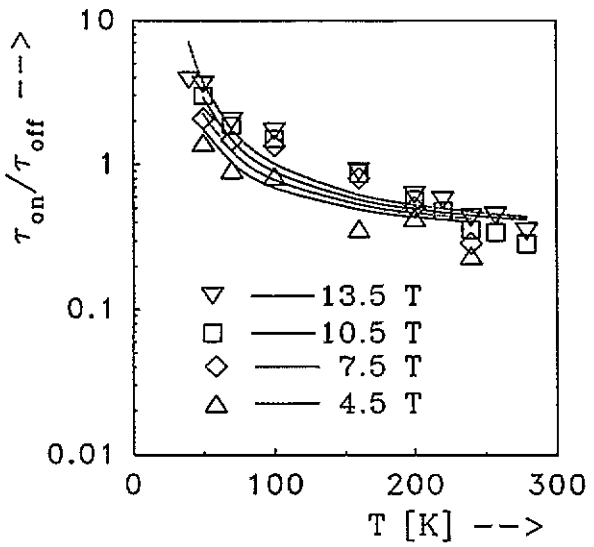

Figure 10. Dependence of τ_{on}/τ_{off} on T for different B_a in $Y(Fe_{0.75}Al_{0.25})_2$. The lines are explained in the text.

According to Boltzmann statistics the ratio of the equilibrium occupation probabilities p_{on} and p_{off} of the two states which are allowed in the model should be

$$p_{on}/p_{off} = \exp(-\Delta S/k_B + \Delta E/k_B T + \mu_{cl}B_a/k_B T) \qquad (1)$$

where it is assumed that $\langle \mu_{Fe} \rangle \ll \mu_{cl}$, and ΔS is the entropy difference and ΔE is the energy difference of the two states for an Fe atom. The equilibrium condition

$$p_{on} w_{on \to off} = p_{off} w_{off \to on} \tag{2}$$

and the definitions of $\tau_{on} = 1/w_{on \to off}$ and $\tau_{off} = 1/w_{off \to on}$ give

$$p_{on}/p_{off} = \tau_{on}/\tau_{off}. \tag{3}$$

This offers the possibility of obtaining information about ΔS, ΔE and μ_{cl} from the values τ_{on}/τ_{off}. Fits of the dependence of τ_{on}/τ_{off} on T and B_a were only successful with values of ΔS, ΔE and μ_{cl} which were restricted to being independent of both T and B_a. As an example the results for $Y(Fe_{0.75}Al_{0.25})_2$ are shown in figure 10. The lines are calculated for different fixed values of B_a using equations (1) and (3) with the fitting results for ΔS, ΔE and μ_{cl}. The correspondence to the values determined from the Mössbauer spectra is not perfect but the values of ΔS, ΔE and μ_{cl} achieved should be reliable enough to give an estimation of the order of the correct values. From this analysis a dependence of these values on T and B_a cannot be excluded but it does not seem to be very extensive. The values of ΔS are between 1.3 and 3.2 k_B, ΔE between 1×10^{-21} and 1.7×10^{-21} J (corresponding to 72 and 123 K) and μ_{cl} between 6.2 and 8.5 μ_B for all samples (for $x = 0.40$ and 0.25 in $Y(Fe_xAl_{1-x})_2$ values could not be obtained because too few measurements were carried out).

Assuming an Fe moment of 1.8 μ_B as measured in YFe_2 [22] and parallel alignment of the Fe moments in the correlated regions gives only three to five Fe atoms per correlated region.

The high number of Fe atoms in correlated regions found by the high values of $\tau_{on}/(\tau_{on} + \tau_{off})$ at lower T and higher B_a can only be explained by a high number of correlated regions. The increase of magnetic order with decreasing temperature means that more correlated regions exist but that their sizes remain more or less constant and that their lifetimes increase with decreasing T.

6. Conclusion

The model employed is suitable to describe the Mössbauer spectra of Fe in the diamagnetic host Au as well as in the Pauli paramagnetic host YAl_2 over a broad range of Fe concentrations and thus seems to be of more general applicability. We plan to check this assumption by further investigations on other spin glasses.

To conclude, the following findings hold for both types of compound investigated for the temperature range $T_f \lesssim T \lesssim 7T_f$.

(i) There exist spatial correlations of spins over times of about 2 to 200 ns in fields of 13.5 T.

(ii) The lifetimes of the magnetic correlations increase with increasing applied field and decreasing temperature but the sizes remain almost constant.

(iii) The applied field and the temperature seem to have little influence on the formation of the correlations.

(iv) The decay of the correlation seems to be an effect of entropy.

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