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Magnetic properties of $Fe_xMn_{0.3}Al_{0.7-x}$ ($0.275 \leqslant x \leqslant 0.525$) disordered alloys

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Abstract. We report on the magnetic properties of $Fe_xMn_{0.3}Al_{0.7-x}$ ($0.275 \leqslant x \leqslant 0.525$) disordered alloys, which were investigated by means of Mössbauer spectroscopy, ac magnetic susceptibility and magnetization measurements. Our results are summarized in a magnetic phase diagram which includes both a re-entrant spin glass–ferromagnetic transition line for $x > 0.425$ and a re-entrant spin glass–antiferromagnetic transition line for $x < 0.375$.

1. Introduction

Disordered alloys in the Fe–Mn–Al system can be considered candidate materials for the occurrence of spin glass (SG) behaviour, due to the presence of competing ferromagnetic (F) and antiferromagnetic (AF) interactions. Furthermore, the existence of some paramagnetic (P) sites could also be the origin of interesting re-entrant spin glass (RSG) behaviour. Pérez Alcázar *et al* [1] showed that, at room temperature (RT), this system evolved, in the body centred cubic (bcc) phase, from ferromagnetism to a P phase when either the Al or the Mn concentrations are increased (a theoretical study by Rosales Rivera *et al* [2] suggested the occurrence of a SG phase in this system). Also, the presence of P and SG phases in the $Fe_{0.5}(Mn_xAl_{1-x})$ series was experimentally shown by Kobeissi [3]. In a recent work, Pérez Alcázar *et al* [4] reported the occurrence of RSG phenomenology in the disordered $Fe_{0.45}Mn_{0.30}Al_{0.25}$ alloy. Finally, Pérez Alcázar *et al* [5] have described a magnetic phase diagram corresponding to the $Fe_xMn_{0.6-x}Al_{0.4}$ series which showed a complex phase distribution including the presence of the P, AF, F, SG and RSG phases.

The aim of the present work is to elucidate, on the basis of Mössbauer, alternating current (ac) susceptibility and magnetization measurements, the possible occurrence of SG, RSG and magnetic clustering in the $Fe_xMn_{0.3}Al_{0.7-x}$ disordered alloys.

2. Experimental details

The samples studied were prepared by melting high-purity Fe, Al and Mn powders in an arc furnace and under an Ar atmosphere. After melting, the resulting buttons were encapsulated in

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evacuated sealed quartz tubes and annealed at 1000 °C for a week to ensure homogenization. Finally, the samples were quenched in icy water to retain the disordered high-temperature structure.

^{57}Fe Mössbauer spectra from the samples with $0.275 \leqslant x \leqslant 0.500$ were recorded at temperatures between 15 and 295 K using a helium closed-cycle cryogenerator and a constant acceleration spectrometer with a ^{57}Co(Rh) source. The experimental system was checked against vibration; the full-width at half-maximum (FWHM) shown by the lines of the magnetic sextet of α-Fe at 15 K was 0.28 mm s^{-1}, whilst at 295 K the FWHM was 0.26 mm s^{-1}. Thus, the increase in the linewidth of the Mössbauer lines introduced by the vibration of the cryogenerator is very low and can be considered negligible. All the spectra were computer fitted using static hyperfine magnetic field distributions. No predetermined shape was assumed for the distributions, which basically consisted of histograms of sextets. The line profile of the individual lines of the sextets of the distributions was assumed to be Lorentzian, with the individual line width fixed at 0.27 mm s^{-1} during the fitting procedure. No correlation was introduced between the isomer shift and the hyperfine magnetic field. All the isomer shifts are referred to α-Fe.

The ac susceptibility measurements were carried out on pressed powder samples (prepared by crushing the quenched buttons) under an ac field of amplitude 3×10^{-4} T, a biasing direct current (dc) field of 0.001 T and at a frequency of 175 Hz. The temperature dependence of the magnetization of the samples with $x = 0.275$, 0.300, 0.400 and 0.500 was measured at low (0.001 T) and high (2 T) magnetic fields, as well as under field cooling (FC) and zero field cooling (ZFC) conditions by using a SQUID magnetometer.

3. Results and discussion

3.1. Mössbauer spectroscopy

All of the RT Mössbauer spectra recorded from the alloy samples with $0.275 \leqslant x \leqslant 0.500$ consisted of a single line with a FWHM of approximately 0.50 mm s^{-1}. The variation of the isomer shift with composition is shown in figure 1. According to this figure, the isomer shift values decrease with increasing Fe content (i.e. with decreasing Al concentration). This means that a decrease in Al concentration brings about a decrease in the electron population of the conduction band and then a decrease in the 3d electron density around the Fe nucleus. If the electron density of the 3d shell of Fe is reduced, the shielding of the s electrons at the nucleus is reduced; therefore, the s electron density increases within the nuclear volume and, consequently, the isomer shift decreases. A similar variation of the isomer shift values with Al concentration has also been observed in other Fe–Al–Mn alloys [3].

The Mössbauer spectra recorded from the $x = 0.275$ alloy between 15 and 295 K shows in all the cases a single line pattern (figure 2(*a*), left). The FWHM at 295 K of this line is 0.52 mm s^{-1}, i.e. about twice as large as that shown by the α-Fe calibration spectrum. This large linewidth cannot be caused by a saturation effect originated by a large amount of sample, since an effective absorber thickness of about 10–15 mg cm^{-2} of natural Fe was used in all the experiments. Thus, the possibility of that singlet being originated by the superimposition of two narrower paramagnetic singlets [3] was considered. However, the spectrum is quite symmetric and the χ^2 value of the two-singlets fit did not improve significantly with respect to that obtained from the one-singlet fit. The origin of the observed broadening at room temperature could be related to the occurrence of disorder in our system: the fluctuation of the local Mn and Al concentrations would give rise to the existence of a distribution of the number of Mn and Al atoms in the nearest coordination shells of the Fe atoms and, thus, to

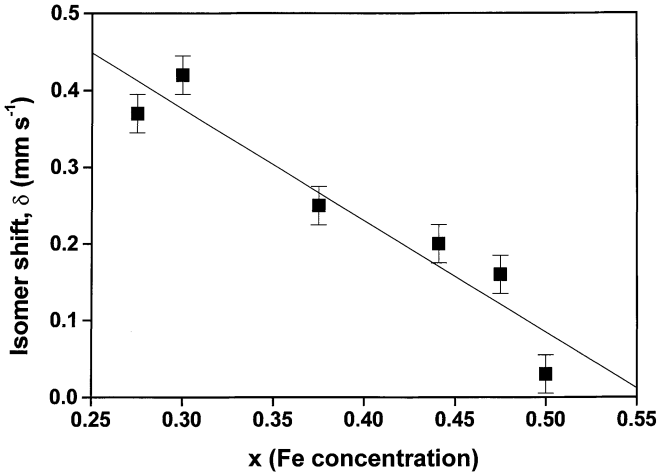
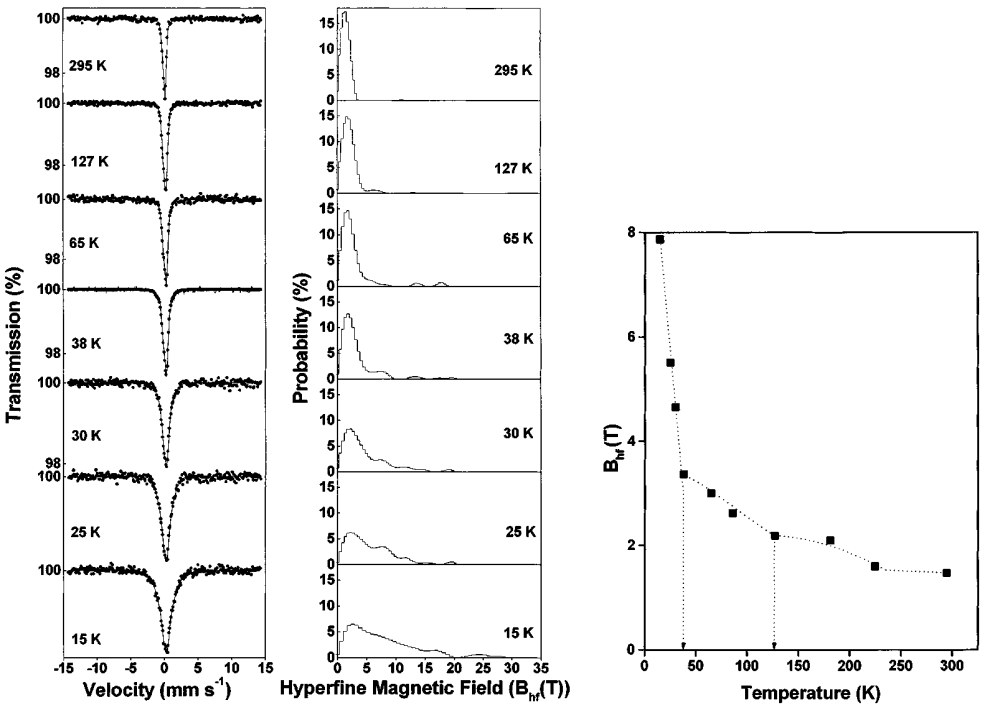


Figure 1. The variation of RT isomer shift with Fe concentration.



(*a*) (*b*)

Figure 2. (*a*) Mössbauer spectra recorded at different temperatures of the $x = 0.275$ sample and the corresponding hyperfine magnetic field distributions. (*b*) The variation of the average hyperfine magnetic field of the distribution with temperature. The broken curves are plotted as guidelines for the eyes.

the existence of a distribution of the Fe sites, characterized by slightly different isomer shifts. This, obviously, would be reflected in a broadened absorption line. However, the evolution of

the FWHM of the Mössbauer line with decreasing temperature (it increases from 0.52 mm s^{-1} at 295 K to about 0.80 mm s^{-1} at 39 K and below 39 K it suffers an abrupt increase, being almost 1.80 mm s^{-1} at 15 K (figure 2(*a*), left)), and the magnetic measurements (see below) lead us to think of the existence of a relaxation process which could occur concomitantly with the disorder of the paramagnetic sites. It must be borne in mind that in addition to the occurrence of disorder, this sample presents a large Al concentration or, in other words, an important magnetic dilution. Thus, at a given temperature, those sites having a larger number of neighbouring magnetic atoms could exhibit (either spontaneously or under the action of a moderate polarizing field) non-frustrated (F and AF) orders as well as frustrated (SG) orders. The nature of the local order depends on the magnitude of the applied field, on the local excess (or balance) of Fe and Mn atoms and on the magnitude of the interactions present. In the following we will refer to those sites as magnetic clusters. In summary, at 295 K, the Fe atoms belonging to the smallest clusters would remain in our samples in the P state whilst those belonging to larger clusters could experience some magnetic order and could be responsible for the observed line broadening. The observed steady increase in linewidth with decreasing temperature may reflect a very gradual ordering of these magnetic clusters [6]. We would remark, however, that, with the present experiments, we cannot decide whether the broadening at RT is attributable only to the disorder in the P sites, magnetic relaxation or both effects.

In order to account for the existence of magnetic ordering and taking into account the likely existence of magnetic clusters of different topologies, all of the spectra were fitted using a hyperfine magnetic field distribution. The results of the fitting are presented in figure 2(*a*). It is clear that the distribution corresponding to the 295 K spectrum shows a sharp peak between 0 and 3 T, with no contributions at higher fields. This suggests that, at this temperature, a large fraction of the clusters remain unpolarized. As the temperature decreases, this peak broadens, its intensity decreases and contributions at higher fields start to appear. This clearly indicates the existence of some degree of cluster polarization at temperatures below 295 K. The distributions corresponding to the spectra recorded below 30 K are much broader, that is, the contribution of larger hyperfine fields is clearly more important; this suggests the presence of disorder in the distribution of the underlying magnetic interactions. The lack in the spectra of well-developed magnetic components (or in other words, the small magnitude of the hyperfine magnetic fields measured) may be a consequence of the important magnetic dilution in this sample, the type of magnetic interactions involved and the existence of magnetic clusters.

The variation of the obtained average magnetic field with temperature is depicted in figure 2(*b*). The resulting curve is not smooth and shows a clear kink at 39 K and a change in slope at about 137 K. We associate the observed steady increase in the magnitude of the average field between 295 K and 127 K to the above mentioned cluster ordering. The change in slope at about $T_N = 127$ K can be related to the onset of the AF order, which is expected to develop in a sample with such a composition [2, 7]. The abrupt increase in the magnitude of the average magnetic field, B_{hf}, below $T_k = 39$ K indicates that a collective magnetic ordering process occurs below this temperature. In fact, the shape of the B_{hf} against T curve resembles that shown by systems displaying RSG behaviour [8–12] and can be understood on the basis of the model proposed by Swaslow and Parker [13] for the interpretation of that type of SG behaviour. According to this model, at T_N a large fraction of the total number of magnetic moments (i.e. those having an adequate number of first magnetic neighbours and not being frustrated) gets ordered, due to the existence of AF exchange interactions. Nevertheless, and due to the occurrence of structural disorder, magnetic dilution and competitive interactions some moments (i.e. those being highly frustrated) would remain in the P state at temperatures below T_N. AT T_k the P spins which are frustrated due to the competitive interactions, would

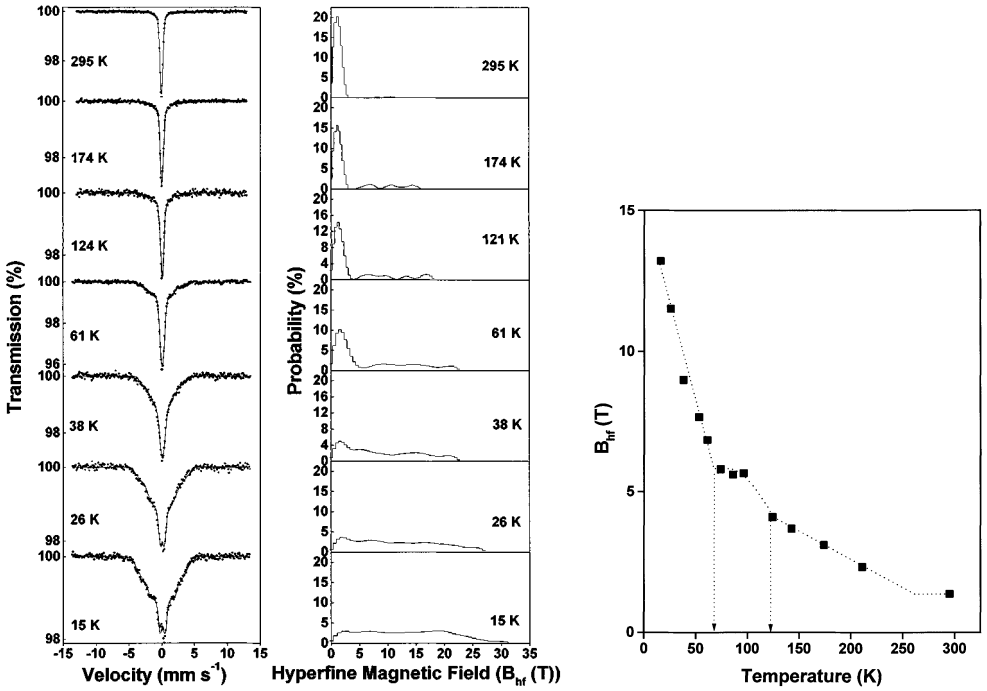


Figure 3. (*a*) Mössbauer spectra recorded at different temperatures of the $x = 0.375$ sample and the corresponding hyperfine magnetic field distributions. (*b*) The variation of the average hyperfine magnetic field of the distribution with temperature. The broken curves are plotted as guidelines for the eyes.

freeze on top of the AF matrix, therefore contributing to the observed average hyperfine field. It is known from the theoretical work of Rosales Rivera *et al* [2] and Zamora *et al* [7] that a RSG can appear in the $Fe_xMn_{0.7-x}Al_{0.3}$ system as a low-temperature phase for intermediate Fe and Mn contents. Therefore, it is plausible to associate the abrupt increase in B_{hf} below 39 K as due to the existence of such a RSG phase. We would also like to mention that the variation with decreasing temperature of the average magnetic field which characterize the Mössbauer spectra recorded from the $x = 0.300$ sample (not shown) is similar to that observed in the $x = 0.275$ alloy: it suffers a small, gradual increase between 300 K and T_k (in this case $T_k = 54$ K) and below this temperature it increases abruptly.

The Mössbauer spectra recorded at different temperatures from the $x = 0.375$ alloy are shown in figure 3(*a*). Similarly to that observed in the $x = 0.275$ spectra, a very gradual increase of the linewidth from 0.52 mm s^{-1} at 295 K to about 0.75 mm s^{-1} at 61 K is observed. However, besides this observed broadening, it is also evident that below 174 K a broad magnetic pattern starts developing at the wings of the single line. This magnetic component clearly dominates the spectra recorded below 61 K. Thus, a fitting approach which included a hyperfine magnetic field distribution was used. The obtained hyperfine magnetic field distributions are shown in figure 3(*a*) and the variation of the calculated average magnetic field with temperature is presented in figure 3(*b*). The curve presented in figure 3(*b*) shows two kinks at approximately 124 K and 67 K. As in the case of the $x = 0.275$ sample, we associate the observed increase in B_{hf} between 295 K and 124 K with the gradual ordering of the magnetic clusters which are also expected to exist in this sample. For the present composition

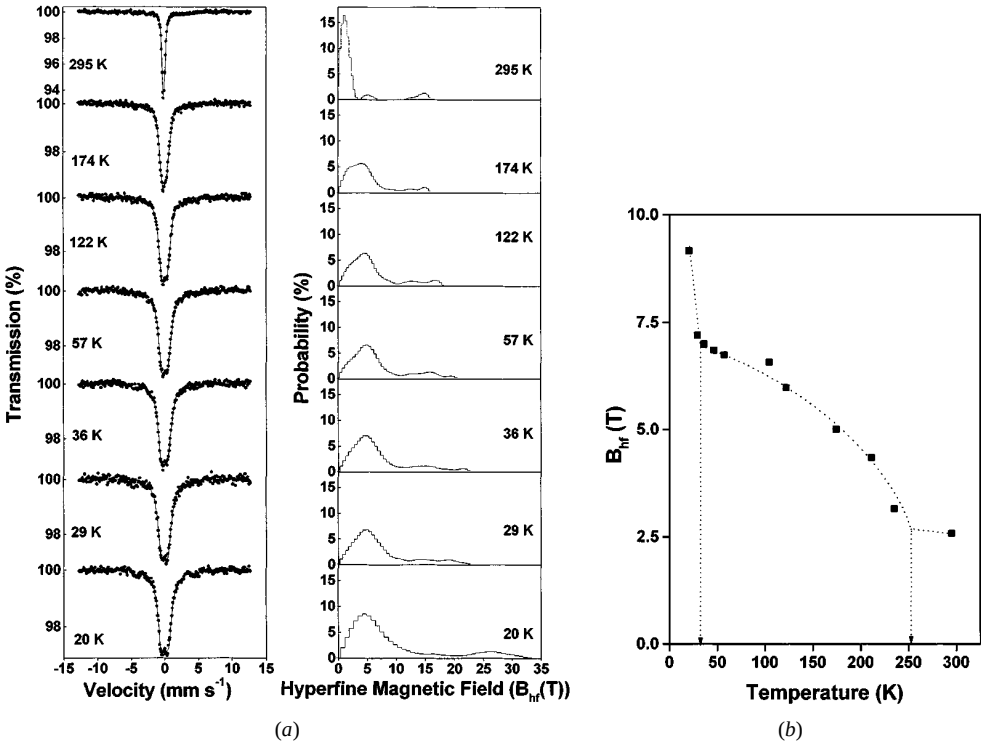


Figure 4. (*a*) Mössbauer spectra recorded at different temperatures of the $x = 0.500$ sample and the corresponding hyperfine magnetic field distributions. (*b*) The variation of the average hyperfine magnetic field of the distribution with temperature. The broken curves are plotted as guidelines for the eyes.

the existence of AF interactions is also expected [2, 7], so the kink clearly observable at 124 K will be associated with the onset of such a type of magnetic order within the solid. Finally, the kink observed at 67 K can be associated with the transition temperature of a RSG phase. It is interesting to note that at a given temperature, the average hyperfine magnetic fields measured in the $x = 0.375$ sample are systematically larger than those observed in the $x = 0.275$ sample. This can be explained by taking into account that the extent of the magnetic dilution in the $x = 0.375$ sample has to be less (in view of its smaller Al content) than that existing in the $x = 0.275$ sample and, therefore, it is more probable to find in the former sample local neighbourhoods having an average number of first neighbours sufficient to stabilize the AF order. The Mössbauer spectra recorded below 50 K from the $x = 0.441$ alloy have a similar shape to those recorded from the $x = 0.375$ sample, and it is noted that its corresponding average hyperfine magnetic field also suffers an abrupt increase below 47 K.

The variation with decreasing temperature of the Mössbauer spectra recorded from the $x = 0.475$ and $x = 0.500$ alloys (results corresponding to the latter sample are shown in figure 4(*a*)) resembles more that shown by the $x = 0.275$ sample than that corresponding to the $x = 0.375$ or the $x = 0.441$ alloys. The presence of the unresolved hyperfine magnetic pattern seen in the latter alloys is not so evident in the case of these two alloys, having the highest Fe contents of the series. Instead, a clear broadening of the spectral line is observed with decreasing temperature. Of course, this broadening must be related to the development of the magnetic order within the solids. According to the results presented in [2, 7] it could be expected that, for the present compositions, these interactions were F in character. The

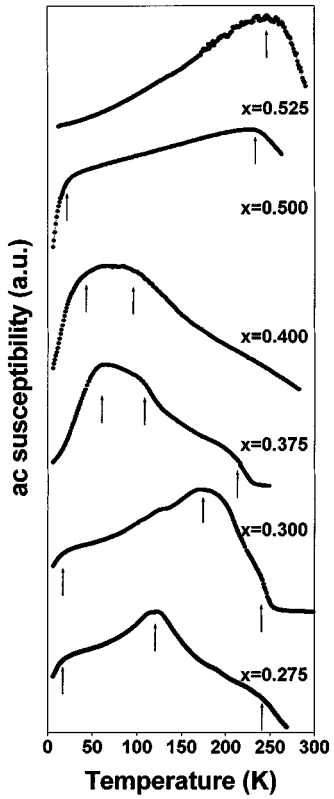
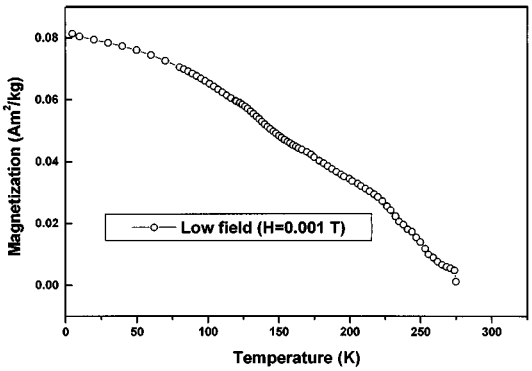


Figure 5. The ac magnetic susceptibility curves for the different samples where x is the Fe concentration.

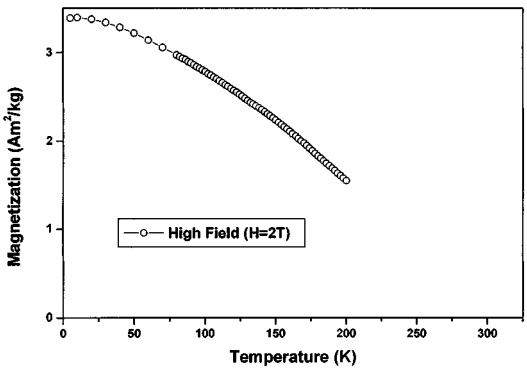
variation with temperature of the magnitude of the average hyperfine magnetic field of the distributions used to fit the Mössbauer spectra of the $x = 0.500$ alloy (figure 4(*a*)) is depicted in figure 4(*b*). Again, a marked increase in B_{hf} is observed below 33 K (41 K in the case of the $x = 0.475$ alloy), suggesting, similarly to the previously discussed cases, the existence of a RSG phase. The kink observed at 253 K can be related to the onset of the F order. It is also interesting to note that a very small, although clearly distinguishable, magnetic component starts appearing in the $x = 0.500$ sample below 36 K.

3.2. Ac magnetic susceptibility

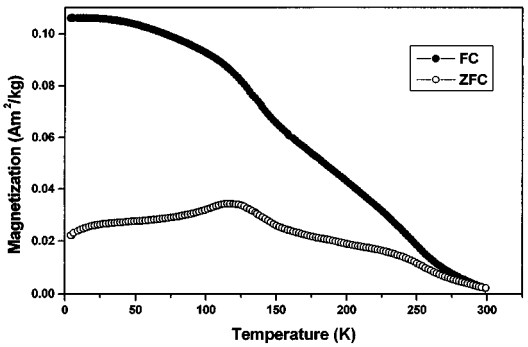
Figure 5 shows the ac susceptibility against temperature curves obtained in samples covering the whole of the compositional range studied. The curves show broad features covering a large range of temperature that suggests the existence, in this system, of a broad range of relaxation times. In fact, these curves resemble those observed in other concentrated RSG systems, in which the existence of distributions of clusters has been reported [9]. The above mentioned features can be described as (partially) overlapping peaks. We associate these peaks with the occurrence of magnetic phase transitions whose critical temperatures are defined as corresponding to the intersection of the lines extrapolating the temperature dependence of the susceptibility at both sides of the peaks. It is interesting to note that all the susceptibility curves show a broad feature at a temperature lying in the range 25–70 K. This feature must correspond to the freezing of the SG phase, whose presence was proposed from the Mössbauer



(*a*)



(*b*)



(*c*)

Figure 6. Magnetization against temperature curves recorded for the $x = 0.275$ sample: (*a*) under 0.001 T, (*b*) under 2 T and (*c*) under 0.001 T and after ZFC and FC of the sample.

spectroscopy results. We would also like to comment that the ac susceptibility curves of the samples with $x = 0.275$, 0.375 and 0.500 (just to mention those samples whose Mössbauer spectra have been presented in detail above) show additional peaks at circa 121 K, 108 K and 233 K, respectively. These temperatures are in the range at which kinks have been observed in the B_{hf} against T plots and must be associated [2, 7] to the transition to the AF ($x = 0.275$ and $x = 0.375$) and F ($x = 0.500$) phases, respectively. The remaining broad peaks appearing, at higher temperatures, in the temperature dependence of the ac susceptibility recorded from

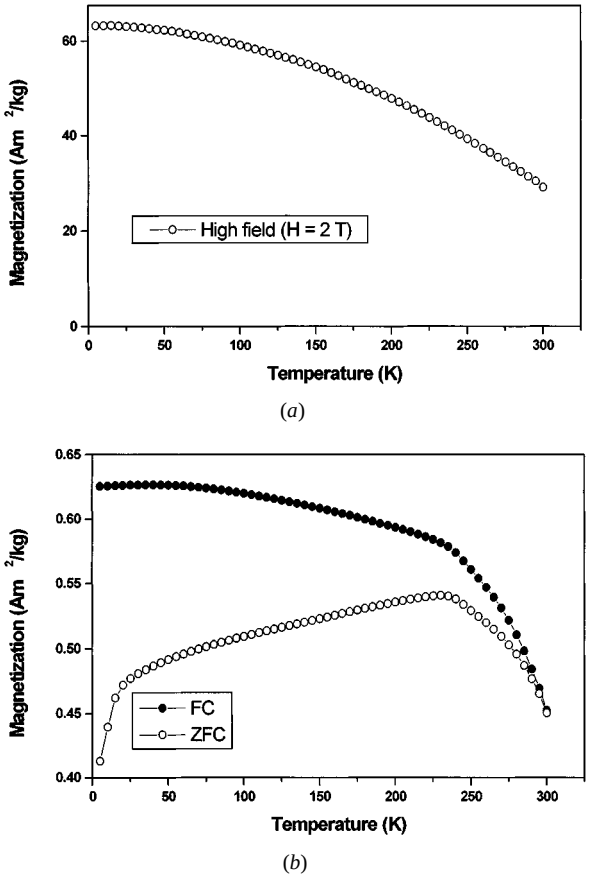


Figure 7. Magnetization against temperature curves recorded for the $x = 0.500$ sample: (*a*) under 2 T and (*b*) under 0.001 T and after ZFC and FC of the sample.

the samples with $x \leqslant 0.375$ (and not apparent from the Mössbauer data obtained under zero applied field) could correspond to the measurement field induced onset of F order occurring, according to their associated temperatures, in the largest Fe-rich clusters.

3.3. Magnetization measurements

In figures 6(*a*) and 6(*b*) the magnetization against temperature curves recorded at low (0.001 T and after FC the sample) and high (2 T) fields, respectively, from the $x = 0.275$ sample are presented. It can be observed that the magnetization values obtained at low fields are small (hundredths of A m^2 kg^{-1}), while those obtained at high fields are large (several A m^2 kg^{-1}) and typical of magnetically ordered materials. In figure 6(*c*) the low-field magnetization curves recorded from the $x = 0.275$ sample under FC and ZFC conditions are presented. The ZFC magnetization dependence on temperature clearly resembles that of the ac susceptibility, showing a well defined maximum at a temperature of about 121 K and a broad feature at about 20 K. A much broader, not so well defined maximum is also observed at about the same temperature in the FC magnetization. We would like to point out the large differences, observed at temperatures above the freezing temperature, between the values obtained in the small- and high-field measurements which, in agreement with our proposal about the magnetic

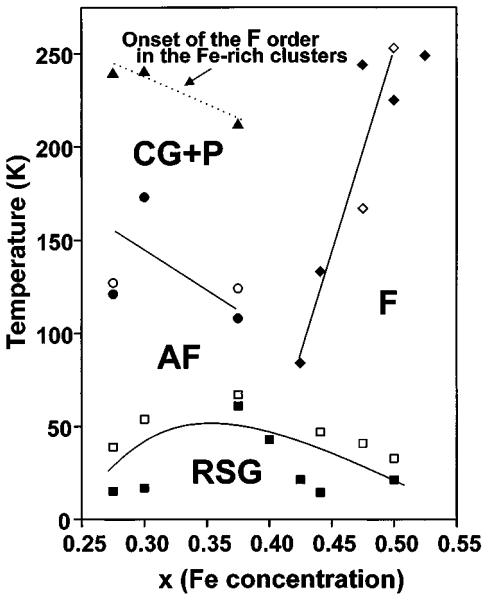


Figure 8. The proposed magnetic phase diagram for the 30 at% Mn alloy series. The full symbols correspond to the ac susceptibility data, the open symbols correspond to the Mössbauer data. The curves are plotted as guidelines for the eyes.

field induction of magnetic order in the $x \leqslant 0.375$ samples, indicates that the system is highly polarizable. We consider that this result is a further indication of the presence of magnetic clusters in our samples. Let us remember in this sense that when the size of a magnetically ordered system is reduced, the ratio of the Zeeman energy (an exclusive function of the number of moments) to the exchange energy (which depends on the amount of moments having, as those on the surface of the system, a reduced number of first neighbours) is increased. Thus, the reduction of the size of the magnetic entities, as that linked to the occurrence of clusters, results in an increase of their polarizability. Similar results to those presented in figures 6(*a*) and 6(*b*) were obtained in the $x = 0.300$, $x = 0.400$ and $x = 0.500$ samples. For example, in the case of the $x = 0.500$ sample, the magnetization recorded at low fields (see figure 7(*b*), where the ZFC and FC curves shown were recorded at a field of 0.001 T) is about two orders of magnitude smaller than that recorded at high fields (see figure 7(*a*)), similar to the case of the $x = 0.275$ sample. The ZFC magnetization dependence on temperature also resembles that of the ac susceptibility, showing a very broad maximum at about 233 K and a broad feature at 16 K. A kink at 233 K is also observed in the FC curve.

3.4. Summary

It follows from the above results that the existence of disorder, competitive interactions and important magnetic dilution gives way to a complex phenomenology in this system. At temperatures slightly below RT, the local fluctuations of the concentration of the Fe atoms lead to the origination of highly polarizable sites capable of displaying a F-like order under the action of small magnetic fields, such as those applied in the susceptibility measurement. Those Fe-rich sites are only observable in the case of the samples exhibiting an AF order due to the fact that the Néel temperature of that long-range ordered phase is lower than the

corresponding, for moderate applied fields, to the onset of the F order within the clusters. As the temperature decreases, the smaller clusters, having fewer Fe and/or Mn atoms, would progressively become more polarizable. Depending on the size and cluster composition, the polarizability could be related in some cases to the volume anisotropy (large, regularly shaped clusters) and, in other cases, to complex surface anisotropies of groups of Fe and Mn atoms (smaller clusters). As the temperature continues to decrease, the thermal energy can diminish until it is less than the exchange energy, and then the paramagnetic background can experience a magnetic phase transition (appearance of collective order, either AF or F, depending on the alloy composition). Finally, at very low temperatures, and as already explained in detail above, the RSG behaviour can appear. RSG behaviour is linked to the spins which, at temperatures above that of the SG freezing transition and due to the occurrence of competitive interactions, get frustrated and fluctuate in a P way between the different orientations, all of them having a similar energy and being separated by low energy barriers.

Thus, we propose the phase diagram presented in figure 8. This phase diagram has been constructed on the basis of our Mössbauer and ac susceptibility results and the theoretical phase diagram proposed by Rosales Rivera *et al* [2] and Zamora *et al* [7], which considers the existence of different phases as F (Fe-rich alloys), AF (Mn-rich alloys), SG (low-temperature phase, intermediate Fe and Mn contents) and P (high-temperature phase, intermediate Fe and Mn contents). It follows from this diagram that a RSG region is observed in all of the compositional range at temperatures below 67 K; an AF region is observed above the RSG region and below 150 K in the Fe-poor region and a F region is observed in the Fe-rich region above the RSG region. In the case of the Mn-rich region of the phase diagram we propose the occurrence, at temperatures above the AF ordering temperature, of polarizable magnetic clusters coexisting with a P phase. In this phase diagram we have included (Al-rich region) the temperatures at which the ac susceptibility data suggested the occurrence of magnetic transitions in large Fe-rich clusters.

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