Non-linear ac susceptibility behaviour of collective
dynamics in heterogeneous nanomagnetic systems

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Abstract. The existence of magnetic systems displaying heterogeneous magnetic structures
is common nowadays. The spin structure is heterogeneous at the nanoscopic level, allowing
the interplay of different magnetic interactions which can include exchange, double-
exchange, RKKY or dipolar interactions. The high degree of spin disorder and/or the
presence of magnetically connected clusters or well-formed grains gives rise to magnetic
relaxation and (or pseudo) collective dynamics. The relaxation behaviour resembles those
observed in archetypal examples such as freezing in canonical (or cluster) spin glasses, and
blocking processes, the latter in a superparamagnetism framework. The AC-susceptibility is
the only in-situ technique covering several (usually 4) frequency decades, providing a full
photograph of the relaxation phenomena. In addition, the AC technique can simultaneously
record the non-linear components which, although of very small magnitude, are of great
sensitivity when detecting subtle magnetic changes, such as phase transitions or the presence
of minuscule magnetic phases. Results of non-linear susceptibility in diverse examples
including reentrant ferromagnets (amorphous FeZr and FeZrCuB), a CMR oxide (a
crystalline LaPb(Mn₀.₈Fe₀.₂)O₃ perovskite) and a GMR FeCuAg alloy (ferromagnetic grains
in a diamagnetic matrix) are reviewed.

1. Introduction
Nowadays, numerous research lines in Magnetism deal with materials, which present a great variety of
potential technological applications (in electromagnetic devices, biomedicine, geophysics and
archaeological, etc.) but with a common nexus, which is the presence of ensembles of magnetic atoms
at the nanometric scale [1-4]. These ensembles are labelled as clusters or grains in a rather undefined
fashion, as sometimes it is not absolutely clear as to whether the size or the presence of clear boundary
limits are the parameters to define them. To cite a few of those, studies of reentrant ferromagnets
(amorphous or crystalline) [1, 5], ultrasoft magnets (some of which are registered as FINEMET® or
NANOPERM®) [6, 7], Colossal Magnetoresistance (CMR) oxides [8, 9], Giant Magnetoresistance
(GMR) granular alloys [7, 10] and fine magnetic particles [11] constitute evident attraction poles. The
fundamental fascination for these materials is based on the fact that the cluster/grain morphology gives
rise to a heterogeneous spin structure and the presence and competition between different magnetic

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interactions (basically exchange, double exchange, superexchange, RKKY and dipolar) in the compound. In this sense, it is still a great challenge to relate the experimental results to a particular spin arrangement and extract quantitative parameters (i.e. canting angles, critical exponents, etc.) in the complex systems mentioned above.

From the crystallographic point of view, the mentioned materials present not only pure crystalline (as, for instance, the CMR perovskite [8]) or amorphous structures (as reentrant FeMnPBa1 or FeZr [5]), but also many of them show intermediate nanostructural states. In the latter, one may include the best soft magnets (FeNbCuSiB or FeZrCuB), which are achieved by crystallising nanometric grains of Fe or Fe(Si) in an amorphous matrix, or the GMR materials, comprising a collection of magnetic crystalline grains in a metallic matrix [6]. On the production side, some of these materials can be produced in thin films or multilayers, with the advantage of a more accurate (and sometimes more simple) interpretation of the experimental data [3]. Nevertheless, it is equally feasible to produce them in large quantities through more conventional chemical [12, 13], solid [14], or melt-spinning techniques [15].

In all these studies, the crucial point to be ascertained is the complex spin (or charge) structure of the compounds, usually formed by a number of clusters/grains (of different sizes and with more or less defined entity) surrounded by a matrix displaying a rich variety of spin structures: random, ferromagnetic (FM), paramagnetic (PM), diamagnetic (DM) or insulating (IN). In addition, there is expected to be a mixture of short- and long-range magnetic interactions among the grains. All those heterogeneous spin structures present similar spin dynamics [11, 16], being difficult to ascribe each of them to conventional magnetic relaxation processes (freezing, blocking, etc.). In figure 1, a sketch of a simplified different situation is shown. In a canonical spin-glass (SG) a sharp transition at the freezing point (Tf) takes place. In more concentrated compounds, an increased degree of clustering is found, resulting sometimes in reentrant behaviour (PM to FM and to SG state, while decreasing in temperature) in which the relaxation is slower at the transition (TRSG). In nanometric grains in an insulating matrix, the relaxation is governed by an Arrhenius-Néel law; no sharp transition is found at the blocking temperature (Tb).

![Figure 1](image.png)

**Figure 1.** Sketch of different heterogeneous spin structures (SG: canonical spin glass with indirect RKKY interaction, CSG: cluster glass of more magnetically concentrated compound, and SPM: non-interacting fine particles) of simple systems in which spins are located at random positions. The magnetic structures present rather similar magnetic relaxation phenomena, according to results observed in macroscopic techniques.

Among the macroscopic techniques, the AC-susceptibility (ACS) is one of the best suited for such a dynamic study. This is due to its intrinsic sensitivity (due to its inherent derivative character) to detect very subtle magnetic transitions and/or different magnetic phases and because when there is a need to define a magnetic relaxation process, it is compulsory to cover several decades of measuring time. Moreover, powerful microscopic techniques (neutron [17-19], Mössbauer [20-22], Muon [23-25] spectroscopies) are constrained to a single measuring time (τ_n ≈ 10^{-14} s, τ_m ≈ 10^{-9} s and τ_μ ≈ 10^{-11} s,
respectively). In contrast, ACS allows results with different measuring times to be obtained (usually between $10^1$ to $10^3$ s, in a SQUID-based susceptometer, or $10^2$-$10^3$ s, in a pick-up coil based set up) in the same sample in exactly identical conditions, and with the easy experimental possibility of adding a biasing $H_{dc}$ field. Here, what is relevant is the use of identical measuring conditions when dealing with samples depending on the magnetic history (the latter being a relevant fact in materials with magnetic irreversibility). Moreover, in heterogeneous spin arrangements, it is advisable to use, not only the real and complex components of the signal (in the linear term), but also the non-linear terms of the susceptibility, obtained if instantaneous lock-in detection of the harmonics is possible.

As a clear example of the usefulness of the ACS technique, we review briefly some straightforward features of the technique with a focus on relevant aspects for the experimental analysis (Section 3). Later, we will discuss results from three systems which, though different on paper, display similar experimental features. While the first two systems are particularly complex and hence the results lack of quantitative definition, the last one is an excellent example of a rather complex system, which can be handled quantitatively and hence, with the possibility of bringing in new issues of discussion. In short, we will start (in section 4) with well-known [6, 20] amorphous FeZr-based metals (Fe$_n$Zr$_{1-n}$ and Fe$_{0.6}$Zr$_{0.4}$CuB$_{1.4}$) of reentrant behaviour, following in section 5 with results for a La$_{0.7}$Pb$_{0.3}$(Mn$_{0.8}$Fe$_{0.2}$)O$_3$ CMR crystalline manganite. This is a member of a family in which the substitution at the Mn$^{3+}$ site by 3d-elements gives rise to a high degree of magnetic disorder (frustration) and an enhanced magnetic clustering tendency [26-29], also making it possible to use Mössbauer spectroscopy by Fe-substitution [21]. The compound in question has been recently analysed microscopically and shows the existence of magnetic glassy behaviour in an insulating (or weakly conducting) matrix [30, 31]. To finish, we will pay attention to results obtained in a representative (and diluted: Fe$_{13}$Cu$_{10}$Ag$_{77}$) GMR granular crystalline member of the FeCuAg system [25], in which we have a coexistence of ferromagnetic grains embedded in a Ag matrix, equally formed by nanometric grains.

2. Experimental Details

The different materials were produced in large (grams) quantities by standard methods. The amorphous metals of Fe$_{91}$Zr$_9$ and a Fe$_{87}$Zr$_6$CuB$_6$ were cast in ribbon-shape by melt-spinning [15] in Ar inside a Bühler apparatus with a quartz crucible at the H. C. Oersted Institute (University of Copenhagen). The La$_{0.7}$Pb$_{0.3}$(Mn$_{0.8}$Fe$_{0.2}$)O$_3$ polycrystalline powders were synthesised by the sol-gel route [32] at the Department of Chemistry of the University of the Basque Country. The last sample, a Fe$_{13}$Cu$_{10}$Ag$_{77}$ powder, was produced by high-energy mechanical alloying in a Fritsch planetary mill in argon-sealed containers at the University College London, following optimised production parameters described in ref. [25]. The composition was checked by EDAX.

The AC-susceptibility ($\chi_{ac}$) was recorded at several frequencies between 4 K and 300 K in a Quantum Design-PPMS magnetometer, allowing the instantaneous recording of the in-phase ($\chi'$) and 90º-quadrature ($\chi''$) components. The samples were warmed up from helium temperatures at steady heating rates, ranging from 0.1 K/min (where peaks were detected) to 2 K/min, in featureless temperature regions. The value of the excitation magnetic field was set between $h = 0.1$ and 10 Oe, depending on the available mass and the response of the material. Special care was taken with the ribbons to apply the $h$ field parallel to the long-axis of the ribbons in order to control demagnetising fields.

3. AC-susceptibility in heterogeneous magnetic systems

The AC-susceptibility ($\chi_{ac}$) is defined as:

$$\chi = \frac{dM}{dH}$$

(1)

The derivative character of the magnetisation M respect to the field H allows subtle susceptibility changes to be detected. The latter are related in practical words to the existence of minute magnetic
phases and of magnetic phase transitions (in general) or freezing and blocking processes, which are commonly found in heterogeneous magnetic systems. The experimental detection is usually carried out through pick-up coils at low (<10^4 Hz) angular frequency \( \omega \), as a voltage \( V \):

\[
V = -na_0\mu_0h\eta
\]  

(2)

where \( n \) is the number of turns, \( a \) is the cross section, \( h \) the oscillating AC-field and \( \mu_0 \) the vacuum permeability. Accordingly, the recorded signal will tend to improve whenever a high frequency is used.

If the \( H \) field oscillates with an amplitude \( h \) at a fixed \( \omega \) and is spatially uniform, then we have:

\[
H = h \cos(\omega t) \Rightarrow M = m \cos(\omega t - \gamma)
\]  

(3)

It is then possible to write:

\[
M = \chi' \cos(\omega t) + \chi'' \sin(\omega t)
\]  

(4)

and the susceptibility is the addition of the real (\( \chi' \)) and complex (\( \chi'' \)) components:

\[
\chi = \chi' + i\chi''
\]  

(5)

The complex susceptibility is associated to energy losses in bulk ferromagnetic materials. The energy losses are usually ascribed to domain-wall processes and have been thoroughly studied [33-35]. When measuring the thermal dependence of \( \chi' \) and \( \chi'' \), we expect to observe a usual \( \chi(T) \) in the DC-magnetisation language, with some influence of the thermal variation of the anisotropy \( K(T) \) at the lower temperatures, if using a very small \( h \) (\( \sim 1 \) Oe). At the \( T_C \) transition, a Hopkinson peak can be observed. In heterogeneous magnetic systems, the existence of clusters or nanometric grains, gives rise to the similar \( \chi(T) \) variations, but usually with a broadened peak at the “transition”. In archetypal SG, the complex susceptibility shows maxima which increase, usually of one order magnitude less than the real counterpart, with the applied frequency.

The variation of frequency is a common procedure to study dynamic relaxation processes and has been explained in [16, 36] and hence will not be covered here in detail. Basically, the analysis consists of several stages, which can be performed realistically depending on the quality of the measurements and/or the complexity of the system (which is high in heterogeneous magnetic systems). If possible, one should start by analysing the temperature shift with frequency of the maxima in \( \chi' \), which provides a straightforward clue to how the system behaves. With this, one can determine the critical dynamics through an Arrhenius-Néel law (typical of SPM), Vogel-Fulcher (phenomenological activation law for glasses) or (less commonly) generalised Vogel-Fulcher. In the next step, a phenomenological Cole-Cole analysis relating the real and complex components can be carried out and get the Argand plot: this allows to extract information about distribution of relaxation times (single or double distributions). This third step requires high-quality data and gives unclear results occasionally, with distributions which are not well-defined. A final approach is to perform the dynamic scaling of susceptibility determining the \( z \) and \( \beta \) exponents of a conventional slowing down process. The latter step is reported continuously for heterogeneous systems in the literature [37].

A less experimentally studied aspect is the use of the results provided by the non-linear susceptibility. It is feasible to develop the susceptibility in a series, including non-linear power terms \( \chi_1, \chi_2, \chi_3, \) etc. [38-40]:

\[
M = M_0 + \chi_1 h + \chi_2 h^2 + \chi_3 h^3 + ...
\]  

(6)
This equation is obviously valid for DC and AC measurements. In the ACS, for the real component (and equally for the complex component, see Ref. [32]) and with the condition that for small applied fields \( h: \chi' h >> \chi^T h \), it is possible to arrive to an expression for the time-dependent magnetisation in which:

\[
\chi^T_1 = \chi_1 + \frac{3}{4} h^2 \chi'_3 + \frac{5}{8} h^4 \chi'_5 + \ldots \equiv \chi_1
\]  

(7)

where \( \chi^T_1 \) is the experimental recorded data, and likewise, \( \chi^T_2 \cdot \chi'_3, \chi^T_3 \cdot \chi'_5, \ldots \) etc. This means that by detecting the different harmonics (at \( \omega, 2\omega, 3\omega, \ldots \)) it is possible to obtain the values of the non-linear susceptibility terms. If \( h \) fields are large (\( h > 5 \) Oe), however, for a precise calculation of the non-linear term \( \chi'_3 \), it might be necessary to include the higher-order experimental signals (i.e: \( \chi'_5, \chi'_7, \ldots \)) as deduced from (7).

The two limiting cases of the magnetic behaviours mentioned in the introduction are found in FM and SG compounds. In a simple ferromagnet there is a spontaneous magnetisation, and the magnetisation \( M \) is effectively the sum of all those non-linear components. In contrast, a SG system has inversion symmetry and hence only odd-powers will appear in the expression (6). In addition, the current theories [41-43] dealing with the SG transitions predict a divergence for the \( \chi'_3 \) term when the applied field \( h \) is small. Besides, it is sometimes possible to extract, if \( \chi'_3(\omega, T) \) data are available, the critical exponent \( \gamma \), if \( zv \) is known, as a consequence of the scaling relation:

\[
\chi'_3 \propto \omega^{-\gamma/zv}.
\]

In the case of a true SPM system, the inversion symmetry of the magnetisation is obeyed as in the SG case, and no even-power terms should appear. Respect to the \( \chi'_3(T) \) component in a non-interacting scheme [44]:

\[
\chi'_3 = -\frac{\varepsilon m_s}{45} \left( \frac{m_s}{k_B T} \right)^3 \int_{\varepsilon m(T)}^{\infty} y^3 f(y)dy + \frac{\varepsilon m_s^2}{60K} \int_{\varepsilon m(T)}^{\infty} f(y)dy; \quad y = V/\langle V \rangle
\]

(8)

where \( \varepsilon \) is the volume fraction occupied by the magnetic nanograins, \( m_1 \) the saturation magnetisation and \( V \) the grain volume. Consequently, the shape of the peak in \( \chi'_3(T) \) should resemble that of the size distribution of particles. In practical terms the width of the \( \chi'_3(T) \) peak should be much larger than that of a conventional SG. A simplified expression for the high-temperature (\( T >> T_g \)) dependence is given by:

\[
\chi'_3 = -\frac{\varepsilon m_s}{45} \left( \frac{m_s V}{k_B T} \right)^3
\]

(9)

Note that the real and complex components would appear in an extra term, as proposed by Raikher and Stepanov [45].

A final possibility, not presented here, is to detect the susceptibility simultaneously with a superposed \( H_{DC} \). This means experimentally that we are detecting not the initial susceptibility but the response at a certain field in the \( M(H) \) variation. The biasing \( H_{DC} \) field is usually small (\( H_{DC} < 250 \) Oe). An obvious observation (often only qualitatively described) is the modification (a reduction in magnitude and shift down in temperature) of the transitions. Apart the qualitative description, the main objective of the analysis is to find out values of the \( \delta \) coefficient through the scaling:

\[
\chi(H_{DC}, T_{max}) \propto H^{\frac{1}{2}\delta-1}.
\]

This hard task is well described using ACS for Ising spin glasses of \( \text{Fe}_{0.5}\text{Mn}_{0.5}\text{TiO}_3 \) [46] and reentrant amorphous alloys of \( (\text{Fe}_{1-x}\text{Mn}_x)_7\text{P}_{16}\text{B}_6\text{Al}_3 \) [47], to mention just two
examples. Nevertheless, it has been performed in most of the cases using DC-magnetisation data, as in polycrystalline ferrite BaCo₆Ti₆O₁₉ [37], or a (La₀.25Nd₀.75)₀.7Ca₀.3MnO₃ perovskite [48] among others.

4. Clusters in amorphous reentrant ferromagnets: Fe₉₁Zr₉, & Fe₈₇Zr₆CuB₆ alloys
One of the best-known examples of reentrant ferromagnets is constituted by the amorphous FeZr-based alloys. Small additions of B (and Cu) modify their Tₐ and TₐSG considerably [49]. Figure 2 shows the ACS for a parent Fe₉₁Zr₉ (Fe₉₁) and a Fe₈₇Zr₆CuB₆ (B₆), the latter being a precursor of well-known nanocrystals. The features in χ' and χ'' are very similar, showing the presence of two transitions (with a sudden drop in χ'') at Tₐ ≅ 211 K (Fe₉₁) and Tₐ ≅ 320 K (B₆), and TₐSG ≅ 21 K and ≅ 10 K for Fe₉₁ and B₆, respectively. Between those transitions, the alloy behaves ferromagnetically. In particular, the complex component presents in Fe₉₁ a very clear shape (with a peak at TₐSG) of a reentrant behaviour.

![Figure 2](image)

**Figure 2.** Ac-susceptibility (real and complex) behaviour (h = 1 Oe, ν = 1 kHz) of a typical amorphous reentrant ferromagnet of Fe₉₁Zr₉ (left) compared to another amorphous alloy of Fe₈₇Zr₆CuB₆ (right), precursor of ultra soft magnets. Tₐ and TₐSG transitions are marked by arrows. Non-linear χ₃' component of both alloys is displayed in the insets. The Fe₉₁Zr₉ alloy shows a clear peak in contrast to the relatively featureless signal of Fe₈₇Zr₆CuB₆.

The usual dynamic analysis [16, 36] based on χ(ω = 2πν, T) provides quantitative and finer results (not shown here). The frequency shift can be quantified as Δ = ΔTₐ / TₐΔ log ν: In the case of a non-interacting ideal superparamagnet, the value of Δ should reach 0.10-0.12. By contrast, typical values for canonical spin-glasses lie around 0.005 – 0.018 [16, 51]. In Fe₉₁, Δ = 0.066(3), an intermediate value in the range of cluster spin glasses, whereas Δ = 0.13(3) in B₆, in the vicinity of a superparamagnetic-like behaviour. In agreement with the relatively low Δ-value, on the one hand, Fe₉₁ obeys a critical slowing down at the transition, with zν = 7.2 and β = 0.7, as explained in detail in ref. [50]. On the other, the FeZrB(Cu) alloys with higher B-content are understood applying a Vogel-Fulcher activation law. All these results seem to point to the fact that increasing the B-concentration not only seems to favour the existence of an extended ferromagnetic matrix, but also the existence of small clusters which relax magnetically as independent entities (compared to the parent Fe₉₁). This interpretation is reinforced here with the results of non-linear susceptibility (see inset of figure 2) in which Fe₉₁ presents a distinct peak at around 30 K in the χ₃' component (of spin glass freezing). This peak is not observed in the relatively featureless χ₃' signal of B₆, in which the ferromagnetic signal is large enough to mask any feeble and broad transition, closer to a blocking behaviour.

The results here correspond to one of the most complicated cases of a heterogenous structure [20]. It is evident the high degree of spin disorder [23, 52, 53] at some length scale and a controversy is still
there [54]. Recent zero and applied field SANS in Fe91 ribbons (including surface contrast analysis) data confirm the view in which nanometric FM clusters coexist with a FM matrix [55]. As commented above, in the FeZr alloys with additions of B [50], the clusters seem to be better defined and behave more independently, as deduced from the dynamic and absence of transition in the non-linear coefficient $\chi''$.

5. Clusters in an insulating matrix of crystalline structure: CMR oxide of La$_{0.7}$Pb$_{0.3}$(Mn$_{0.8}$Fe$_{0.2}$)O$_3$

The ACS technique is increasingly being employed to analyse the CMR-oxides [27, 56-63]. In figure 3, we display a set of plots containing the ACS results for the La$_{0.7}$Pb$_{0.3}$(Mn$_{0.8}$Fe$_{0.2}$)O$_3$ compound.

![ACS plots](image)

**Figure 3.** Left: Thermal variation of $\chi'$ and $\chi''$ ($h = 10$ Oe, $\nu = 1$ kHz) in a highly-magnetically frustrated La$_{0.7}$Pb$_{0.3}$(Mn$_{0.8}$Fe$_{0.2}$)O$_3$ perovskite. The real component displays only a single maximum. There is an improved resolution in the complex component. The behaviour resembles that of Figure 2, with very close values of $T_{RSG}$ and $T_c$. Right: The non-linear component $\chi''$ confirms the presence of both transitions (at around 50 K and 65 K) and unveils a broad hump at 100 K.

As it can be seen, the $\chi'$ component shows a single broad peak centred around 70 K. This peak is somewhat misleading (it seems a single transition) when observing the two-peaked variation of $\chi''$. The latter curve resembles that in FeZr(CuB) alloys described in section 3, with the difference that in this case the $T_{RSG}$ ($\approx 50$ K) and $T_c$ ($\approx 66$ K) transitions are very close. This behaviour, which stems from a cluster-glass spin structure, has also been reported not only in other families of CMR-oxides doped with 3d-elements at the Mn$^{3+}$ site, such as La$_{1-x}$Ca$_x$Mn$_{1-y}$Fe$_y$O$_3$ [27], La$_{0.7}$Ca$_{0.3}$Mn$_{0.7}$Co$_{0.3}$O$_3$ [29] and La$_{0.46}$Sr$_{0.54}$Mn$_{1-y}$Cr$_y$O$_3$ [63], but also in very different perovskite families of Nd$_{1-x}$Sr$_{x}$MnO$_3$ [57], La$_{1-x}$Nd$_x$Mn$_{1-y}$Fe$_y$O$_3$ [58] and La$_{0.46}$Sr$_{0.54}$Mn$_{1-y}$O$_3$ [62] single crystals, among others. Figure 3 also depicts the non-linear component $\chi''$, which displays three distinct features: a negative peak at $\approx 50$ K, a sharp maximum at $\approx 65$ K and a broad hump at $\approx 100$ K. The first two correspond to the $T_{RSG}$ and $T_c$, respectively. The addition of Fe$^{3+}$ at the Mn$^{3+}$ sites provokes the presence of antiferromagnetic coupling of superexchange (SE) nature. The random arrangement of the cation Mn$^{3+}$/Fe$^{3+}$ substitutions and the competition with the double-exchange (DE) FM coupling results in a highly frustrated magnetic structure [26], where a frozen state is favoured at low temperatures. Moreover, the unusually large high-temperature hump can be related to the presence of a progressive (while decreasing T) coherence of spin fluctuations resulting in magnetic clustering [30, 31]. This could be similar to the glass transition (labelled as a T*) in the polaron dynamics reported in La$_{1-x}$Sr$_{x}$MnO$_3$ using inelastic neutron scattering [18]. Hence, the non-linear susceptibility enables the observation of a very fine magnetic process. At $T_c$, the spatial coherence is large enough to establish a long-range FM order. The magnetic structure would then present some degree of clustering, which has been studied by microscopic techniques as muon relaxation, SANS and polarised neutron diffraction [30, 31]. The
issue on whether a phase separation (PS) is formed and, if present, whether the PS takes place at µm length scale or at very local ranges (nanometric clusters) is still an issue of enormous interest and controversy [64]. In this sense, very recent results based precisely on ACS measurements report about different concepts such as disorder-induced spin glass state and nanometric orbital charge order without PS in high-quality Eu_{0.5}Ba_{0.5}MnO_{3} single crystals [65] and self-generated magnetic colloid in (La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_{3} [48]. In the present Fe-doped perovskites, any frequency-dependent ACS analysis would provide relatively large delta values. To study the exponents, a very strong experimental effort (with small excitation fields and extremely narrow critical region for temperatures) is needed to observe the variation in the critical exponents (zv and β) in a critical slowing down approach. Even if the exponents provide correct values, it would be a valuable task to quantify the number of spins effectively participating in the transition. This would provide a novel procedure to establish the existence of clustering [66]. This is a promising study which is being presently carried out on a series of La_{0.7}Pb_{0.3}(Mn_{1-x}M_x)O_{3} M = Fe, Co and Ni compounds.

6. Ferromagnetic crystalline grains in a diamagnetic matrix: GMR alloy of Fe_{13}Cu_{10}Ag_{77}

In this case, we can go through the whole analysis since this heterogeneous system, while of intermediate character between an ideal SPM and a CSG, allows quantifying parameters with the results at hand. From the structural point of view, the representative alloy Fe_{13}Cu_{10}Ag_{77} comprises 4-5 nm Fe(Cu) nanograins embedded in a diamagnetic metallic Ag matrix, as has been carefully studied by Scanning Transmission Electron Microscopy (STEM), multipattern analysis of combined Mo-Kα, Cu-Kα and λ = 1.23 & 2.34 Å neutron powder diffraction data and Small Angle Neutron Scattering (SANS) at zero and applied magnetic field [67].

Figure 4. In-phase χ'(T) and Out-of-phase χ''(T) for the granular alloy Fe_{13}Cu_{10}Ag_{77} measured with an applied oscillating magnetic field \( h = 10 \) Oe and for \( v \) between 10 Hz and 10000 Hz. The blocking temperatures (\( T_B \)) correspond to the maxima. Note that \( T_B \) shifts to higher temperatures with increasing frequency.

This structure gives rise to a superparamagnetic behaviour in which the net magnetic moment of each single domain grain follows a Néel thermal relaxation dependent on the energy barrier, which is overcome in the spin-flip process [11]. This energy barrier is related to the anisotropy (K) and volume (V) of the grain (\( E_n = KV \) in uniaxial anisotropy). For low temperatures (\( T << T_B \)), the grain moments appear blocked in the anisotropy directions of each grain and for high temperatures (\( T >> T_B \)) the system behaves as a paramagnet with very high magnetic moments. It is worth noting that the blocking process is individual of each grain but, for high concentrations of Fe(Cu) grains, the grains are so close to each other (a few nm) that they could interact through dipolar or RKKY interactions.
These interactions would modify the magnetic behaviour of the system, introducing a collective component in a similar way to the one that originates the freezing in a cluster spin-glass system.

From measurements of the linear AC-susceptibility \( \chi'(T) \), \( \chi''(T) \), shown in figure 4, the shapes of the curves presented by a SPM and a SG are very similar, it only being possible to distinguish them through the frequency dependence of the blocking/freezing temperature, as mentioned earlier. For the Fe\(_{13}\)Cu\(_{10}\)Ag\(_{77}\), \( \tau_0 = 0.036(6) \) in nearly 4-decades. As it is shown, the obtained values do not correspond to the ones characteristic of an ideal SPM. This gives a clear cut indication that distances among the Fe(Cu) grains are of such small size that magnetic interactions through the metallic matrix are macroscopically evident. Another indication of the influence of inter-particle interactions in the dynamics of the sample comes from the increasing with frequency of the height of the peak in \( \chi''(T) \) whereas it is almost constant with frequency for a non-interacting system [45, 68].

In order to characterise the magnetic dynamics of the alloy, the relaxation process of the grain moments has been initially fitted to a SPM Arrhenius-Néel law. However, the obtained results lack of physical meaning (\( \tau_0 = 10^{-30} \) s), and consequently the behaviour is not that of a non-interacting SPM. To quantify the effect of the interactions, it is possible to use the Vogel-Fulcher expression [16] in the form:

\[
\tau = \tau_0 \exp \left( \frac{E_B}{k_B(T - T_0)} \right)
\]

where \( T_0 \) has been introduced as an additional parameter with respect to the Arrhenius-Néel expression (\( \tau \), relaxation time; \( E_B \), energy barrier) representing the temperature for which the relaxation time diverges. The large value of \( T_0 \) (84 K for \( \tau_0 = 10^{-6} \) s) obtained for Fe\(_{13}\)Cu\(_{10}\)Ag\(_{77}\) clearly confirms that the magnetic interactions among the grains are giving rise to collective behaviour. In this sense, it is necessary to analyse the magnetic behaviour of Fe\(_{13}\)Cu\(_{10}\)Ag\(_{77}\) in terms of collective dynamics, and to study the existence of a continuous phase transition. This is characterised by the divergence of the spin correlation length (\( \xi \)) when the phase transition temperature (\( T_0 \)) is approached from \( T \to T_0^- \) as

\[\xi / a = (T/T_0 - 1)^{-\nu},\]

\( a \) being the average distance between interacting moments and \( \nu \) a critical exponent. According to conventional critical slowing down, the relaxation time due to correlated dynamics (\( \tau \)) is related to the correlation length as

\[ \tau \propto (\xi / a)^z, \]

where \( z \) is the dynamic critical exponent. Hence, \( \tau = \tau_0 (T/T_0 - 1)^{-\nu} \) with \( \tau_0 \) the microscopic relaxation time [16]. Our results provide a reasonable fitting with \( \nu = 9(1) \), \( T_0 = 84 \) K and \( \tau_0 = 10^{-5} \) s in this granular interacting alloy. This is a sign that the interactions are strong enough to permit a cooperative behaviour at the transition. This result is in agreement with recent reports in interacting FeC (\( \approx 5 \) nm) ferrofluids [69] with different volume concentrations (0.06, 5 and 17 %) due to dipole-dipole interactions.

To throw extra light onto the relaxation behaviour, we continue with the analysis noting that the linear susceptibility can be reproduced by the Wohlfarth superparamagnetic approach, under certain considerations, for both a SPM and SG system [44]. This fact has given rise to different interpretations in which the possibility that the spin-glass freezing would not be a phase transition but a progressive freezing of the moments of SPM clusters has been considered. However, Bitoh et al. [44] established that the blocking model cannot explain the divergent behaviour of the non-linear term, \( \chi''(T) \) in a SG.

In our case, as is shown in figure 5 (left), the broad peak that appears in \( \chi''(T) \) resembles the characteristic one of a SPM, it being very different to the divergent behaviour commonly obtained for
SG. However, the temperature for which $\chi_3'(T)$ reaches its minimum value is related to $T_B$ and is much higher ($\simeq 4$ times) than the one expected ($\simeq 25$ K) for Fe(Cu) nanograins of 4-5 nm of diameter [70]. The reason for this shift in temperature is again the presence of magnetic interparticle interactions, the magnetisation reversal process being then more difficult. In figure 5 (right), $\chi_3'(\nu, T)$ values are shown. At certain values of $\nu$ (50, 1000 and 4000 Hz), a maximum in $\chi_3'(T)$ is evident. Previous work in nanosized maghemite $\gamma$-Fe$_2$O$_3$ particles with a different volume concentration (from 0.3% to 17%) has related the appearance of this maximum with the existence of dipolar interactions among the magnetic nanograins in the sample [71]. We expect the dipolar interactions, in agreement with theoretical calculations [72] and experimental ACS data in CoCu GMR alloys [73], to be much more intense than RKKY in this low-concentrated (13% at. Fe) metallic alloy.

To fit the $\chi_3'(\omega, T)$, given the certain presence of interaction, it is better to use the simplified expression for temperatures well above the blocking temperature ($T >> T_B$), given in (9), where $\chi_3'(T) \propto T^{-3}$. This dependence on $T^3$ is evident in our alloy (see figure 6, left) for high

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**Figure 5.** Left: $\text{Fe}_{13}\text{Cu}_{10}\text{Ag}_{77} \chi_3'(T)$ at $\nu = 300$ Hz and different oscillating fields $h$ (0.2 to 1 Oe). Note that the signal tends to decrease when the field increases. Right: $\chi_3'(T)$ at $h = 10$ Oe and $\nu = 50-4000$ Hz. A positive peak at around 40 K appears for certain values of the frequency.

**Figure 6.** Left: $\chi_3'$ for $h = 10$ Oe and $\nu = 50$ Hz. The solid line shows the SPM dependence of $\chi_3'$ with $T^3$ for $T >> T_B \simeq 100$ K. Right: $\chi_3'_{\text{max}}$ vs. field at $\nu = 300$ Hz. This plot shows the divergence nature of $\chi_3'$ in the limit $h \rightarrow 0$ as expected for a SG.
temperatures (close to RT) and the free spin-flipping process of net moments of the grains is exactly the same as the one in a typical SPM. No measurements for T > RT have been recorded, as the structure of the nanometric FeCuAg might be modified, and produce an agglomeration of grains, the latter being a common feature in metastable granular alloys [25, 74].

Moreover, if $h$-dependent data are available (see figure 6, right), it is possible to observe the behaviour of $\chi_3'$ for $h \rightarrow 0$ ($h \cdot 0.1$ Oe). To avoid undesired errors in the magnitude of the $\chi_3'$ ($h$) values due to field effects, the values have been corrected of the possible influence of $\chi_3'$ ($h$) (higher-order term). In our case, the data seem to diverge, similarly to a SG, as has been recently found in a comparison between SPM and SG compounds of LiNi$_x$O [75]. However, in that work it is also found a $v$ divergence of $\chi_3'$, which does not appear for this Fe$_{90}$Cu$_{10}$Ag$_{77}$ alloy (not shown). The origin of this behaviour is not clear so far, but the fact that the dynamics is governed by a critical slowing down and that the divergence in $\chi_3'$ is present (in $h$-field dependence) point to a behaviour very close to a CSG. It might also occur that, as it is the case in the previously (section 5) described perovskite system, the application of a field induces an enhanced (or extra) coupling between the grains, giving rise to a more spin-glass-like behaviour. In some way, the claim of a self-generated magnetic colloid for CMR-oxides [48] is also valid in the FeCuAg alloy. A comparison with other more concentrated alloys in the FeCuAg system is presently underway.

7. Final comments and Conclusions

The three reviewed examples of heterogeneous magnetic systems show different degrees of complexity. The reentrant amorphous ferromagnets are the most complex since the existence of nanometric FM clusters in a FM matrix demands that there be an analysis of very fine details in the experimental data in order to detect their behaviour. In this sense, the magnetic contrast between the clusters and the matrix is feeble due to the existence of a similar FM coupling, varying only in coupling intensity (Bethe-Slater curve) due to the existence of density fluctuations. Even so, it has been possible to define the critical dynamics and, through the non-linear susceptibility, the unambiguous existence of a low temperature spin glass state in Fe$_{90}$Zr$_{10}$. This is clearly modified for the Fe$_{77}$Zr$_{13}$Cu$_7$ alloy, with less interacting clusters. On the other hand, the most simple case is the GMR FeCuAg alloy, where the relatively close (few nm) FM grains in a DM matrix make the existence of interparticle interactions possible and hence the observation of collective dynamics. The dynamics seems to obey a critical behaviour and the non-linear component shows a clear peak, also underlining the fact that the interactions do exist. In an intermediate position in complexity, the DE-SE manganite system in an insulating matrix shows the existence of three nearly simultaneous (in temperature) processes, surely dependent on the applied field (enhancing or suppressing the spin coherence length of clusters) and caused by phase separation at some length scale. The non-linear susceptibility is of paramount importance to observe three such transitions. To some extent, we are in a situation already found 20 years ago when defining the intimate behaviour of spin glass systems. It was certainly necessary to establish a classification of the diverse SG systems, and the carrying out of this task produced remarkable results, with the identification of the CSG and SG behaviours by Souletie and Tholence [76] and of SPM and SG by Dormann et al [11]. Theoretical expressions for non-linear susceptibility have also been worked out [45, 77] using the Fokker-Planck equation in the overdamp case, but analytical solutions are limited when dealing with non ideal heterogeneous systems. It is possible that transitions in heterogeneous magnetic materials might become classified using a new universality class with new effective critical parameters or even that the classification might come from the number of spins participating in the transitions. These are just unexplored suggestions of future work with the ACS data.

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