Magnetic inhomogeneities inherent to spin systems with quenched random-exchange disorder

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A critical assessment of theoretical models proposed in the literature for the spin structure in amorphous Fe$_{100-x}$Zr$_x$ alloys (a three-dimensional ferromagnet with quenched random-exchange disorder which exhibits a re-entrant behaviour at low temperatures), based on a detailed comparison between theoretical predictions and available experimental results, is presented. The infinite ferromagnetic matrix plus finite ferrromagnetic spin clusters model, originally proposed by the author, is shown to provide a coherent basis for understanding the nature and origin of magnetic inhomogeneities in this system.

The past decade has witnessed a growing experimental evidence to the effect that magnetic inhomogeneity or the so-called ‘magnetic microstructure’ is an attribute inherent to magnetic systems as disparate as ferromagnets or antiferromagnets with or without quenched random-exchange disorder, nanocrystalline soft magnetic alloys, nanostructures, magnetic fine particles, granular giant magnetoresistance (GMR) materials, colloidal magnetoresistance (CMR) manganates and frustrated pyrochlore oxides, and that the nature of magnetic inhomogeneity basically decides the magnetic behaviour of a given system. Attempts to understand the origin of magnetic inhomogeneities in these systems have heavily drawn upon the existing knowledge about the influence of spin frustration and local magnetic anisotropy on the magnetic order in the amorphous (a-) Fe$_{100-x}$Zr$_x$ ($7 \leq x \leq 12$) alloys. However, despite the fact that the a-Fe-Zr system is the most thoroughly studied quenched random-exchange ferromagnet (note that this class of ferromagnets includes both quenched random site-diluted and bond-diluted ferromagnets), such attempts have met with limited success primarily because conflicting opinions prevail about the nature and origin of magnetic inhomogeneity and about the finer details of the magnetic microstructure in a-Fe$_{100-x}$Zr$_x$ alloys. Now that the progress in understanding magnetic properties of a wide variety of spin systems is directly linked to the advances made in ascertaining the actual role of competing interactions in the model system a-Fe-Zr, this paper makes a critical assessment of these divergent viewpoints in the light of the existing experimental data. In this context, the results of recent neutron scattering experiments that have provided a crucial clue about the nature of magnetic inhomogeneities in a-Fe$_{100-x}$Zr$_x$ alloys are also briefly discussed.

Bulk magnetization$^{2,5,11,12}$, magnetic susceptibility$^{3,6,10,14}$, Mössbauer effect$^{19-22}$ and muon spin relaxation$^{33}$ data have established the following widely-accepted magnetic phase diagram (Figure 1) for a-Fe$_{100-x}$Zr$_x$ alloys. Barring the alloy with $x = 7$ ($x = 12$), which behaves as a spin glass (conventional ferromagnet) with a well-defined freezing temperature $T_f$ (ordering temperature $T_C$), the alloys with $x = 8-11$ exhibit two transitions as the temperature is lowered from high temperatures; a paramagnetic (PM) to ferromagnetic (FM) transition at the Curie temperature $T_C$ followed at a lower temperature $T_{RE}$ by a transition from the FM state to the reentrant (RE) state. With $x$ decreasing from $x = 11$, $T_{RE}$ increases while $T_C$ decreases such that the $T_{RE}(x)$ and $T_C(x)$ phase transition lines meet at $T_f$ for $x = 7$. There is a general consensus that the RE state is a mixed state in which long-range ferromagnetic order coexists with the spin glass order but the exact nature of the ferromagnetic and spin glass order remains a highly controversial issue.

The next section briefly summarizes the models proposed in the literature for describing the ferromagnetic and re-entrant states in a-Fe$_{100-x}$Zr$_x$ alloys.

Figure 1. Magnetic phase diagram for amorphous Fe$_{100-x}$Zr$_x$ alloys compiled using the bulk magnetization (BM), ac susceptibility ($\chi_{ac}$), Mössbauer effect (ME) and muon spin resonance/relaxation ($\mu$SR) data available in the literature.
Models for magnetic microstructure

Magnetic inhomogeneities in a-Fe$_{100-x}$Zr$_x$ alloys have found four different model descriptions in the literature. The first approach$^{2,4,6,9}$ considers the magnetic microstructure of the samples as consisting of spin clusters of antiferromagnetic (AF) Fe spins and the ferromagnetic (FM) Fe-Zr matrix (in which these clusters are frozen in random orientations for $T \leq T_{RE}$) and arising from the changes in the sign of the exchange interaction due to local variations in the composition (i.e. the sample regions where Fe atoms have predominantly Fe neighbours, Fe spins are coupled antiferromagnetically whereas the Fe spins in the spatial regions where Fe atoms share Zr neighbours they are ferromagnetically coupled), as shown in Figure 2. According to the second (the so-called FM cluster-FM matrix) model, proposed by Kaul et al.$^{3,12,20,23,24}$ and depicted in Figure 3, the spin system for $T \leq T_C$ comprises the infinite three-dimensional ferromagnetic network (matrix) and finite spin clusters (composed of a set of non-collinear but ferromagnetically coupled spins), which are embedded in the spin-canted FM matrix$^{3,12,20,23,24}$ and frozen in random directions $T \leq T_{RE}$. Contrasted with the first picture, the spatial segregation of finite FM clusters and FM matrix in this model originates from the local atomic density fluctuations. A somewhat similar model, put forward by Kiss et al.$^{11}$ based on the interpretation of the magnetization-ferromagnetic field isotherms in terms of the classical theory for interacting superparamagnetic particles, indicates that the FM clusters occupy the entire volume of the sample. The third model regards the a-Fe$_{100-x}$Zr$_x$ alloys to be a ‘wandering axis’ ferromagnet$^7$ (Figure 4) in which the non-collinear magnetic moments are ferromagnetically correlated but the local ferromagnetic axis changes throughout the sample. The fourth one (the so-called transverse spin-freezing model), due to Ryan et al.$^{21,32,33}$, envisages the spin system for $T \leq T_C$ to be composed of ferromagnetically correlated longitudinal ($z$-direction) spin components and strongly fluctuating transverse ($xy$) spin components (Figure 5); as the temperature is lowered below $T_C$, transverse spin components cooperatively freeze in random orientations in the $xy$-plane at $T \equiv T_{RE} \leq T_{xy}$ and coexist with collinear ferromagnetic order along the $z$-direction.

In subsequent sections, the predictions of these phenomenological models are compared with experimental findings with a view to ascertain which of the models forms a correct description of the magnetic inhomogeneities in a-FeZr alloys.

Experimental observations

A variety of experimental techniques such as bulk magnetization$^{2,5,7,14}$ (BM), ‘in-field’ and ‘zero-field’ ac susceptibility$^{3,6,10,12,14}$ (ACS), vibrating reed$^{15}$, electrical and galvanomagnetic transport$^{16,17}$, electrical noise$^{18}$, ‘zero-field’ and ‘in-field’ Mössbauer spectroscopy$^{19-22}$ (MS), ferromagnetic resonance$^{23,24}$ (FMR), small-angle neutron scattering$^{25-28}$ (SANS), inelastic neutron scattering$^9$ (INS), spin polarized neutron scattering$^{30}$ (SPNS), neutron depolarization$^{31,32}$ (ND), muon spin resonance$^{33}$ (SR), Lorentz electron microscopy$^{34}$ (LEM) and Kerr effect$^{35}$ have been employed in the literature to extensively study the approach-to-saturation$^{5,7,11,12}$ (high-field susceptibility), quantum corrections
to electrical resistivity at low temperatures, magnetic excitations, and magnetic irreversibilities, the freezing of the spin degrees of freedom and the softening of spin wave modes are associated with the transition to the reentrant state, magnetoeelastic effects, critical phenomena, electrical noise, and domain structure in α-FeZr alloys. The following observations have been made based on these studies: (i) While the technical saturation in magnetization at all temperatures below the Curie temperature, $T_C$, in reentrant systems is achieved typically at fields $\leq 10$ kOe, the magnetization continues to increase gradually as the external magnetic field, $H$, is increased to values as high as 140 kOe and the magnitude of the high-field susceptibility, $Z_{hf}$, remains essentially unaltered as the temperature is lowered through $T_{RE}$ (the temperature at which the transition to the reentrant state takes place). (ii) Spin wave excitations (propagating transverse spin fluctuations) at low temperatures, enhanced fluctuations in the local magnetization (non-propagating longitudinal and transverse spin fluctuations) over a wide range of intermediate temperatures and for temperatures close to $T_C$ are mainly responsible for thermal demagnetization of the spontaneous as well as in-field magnetization. A partial substitution of Fe by Co or Ni leads to a transformation of other type till the sample warms up to $T_C$ and then disintegrates/disorders them for $T > T_C$ with the result that the average size reduces and the size distribution narrows down. In addition, the Mössbauer and ferromagnetic resonance results demonstrate that the freezing of finite spin clusters in random orientations does not begin at $T_{RE}$ but at a temperature $T = 3.5$ $T_{RE}$ and proceeds gradually over a wide temperature range from $T = 3.5$ $T_{RE}$ down to the lowest temperature. By contrast, the Mössbauer and SR results indicate a cooperative freezing of transverse spin components at $T = T_{RE}$ and place an upper bound of 3% on the sample volume in which unordered spin clusters could exist for $T < T_C$. (vi) The spin-spin correlation length diverges at $T_C$ and the critical behaviour near $T_C$ is akin to that in a three-dimensional Heisenberg ferromagnet. However, unlike a conventional homogeneous ferromagnet, only a small ($5-10\%)$ fraction of the total spins actually participate in the ferromagnetic (FM)–paramagnetic (PM) phase transition, which implies that a small number of spins constitute the infinite FM network (matrix) while a vast majority of the spins reside in the finite FM clusters for temperatures close to $T_C$. (vii) Large ferromagnetic domains (typical size 50 μm), which remain unaltered in size when the temperature is lowered through $T_{RE}$ to temperatures as low as 1K, have been directly observed by Lorentz electron microscopy and Kirk-effect method.

In the next section, we discuss the above observations in the light of the models proposed in the literature and described in the preceding section.

**Inferences**

While the presence of an infinite ferromagnetic matrix for $T < T_C$ and hence the divergence of the spin-spin correlation length, $\xi$, at $T = T_C$ rules out descriptions such as the ‘wandering-axis’ ferromagnet, since in such a ferromagnet, $\xi$ does not diverge at $T = T_C$. The presence of clusters, and that too in a great proportion, is in direct contradiction with the transverse spin-freezing model because it considers the spin system to be magnetically homogeneous even on the microscopic scale. By comparison, the
conclude that in direct contradiction with the proposal of Wildes et al.\textsuperscript{20,22} (Figure 3), which envisages the spin system for $T \leq T_C$ to be composed of the \textit{infinite} three-dimensional \textit{ferromagnetic network (matrix)} and finite spin clusters (composed of a set of \textit{non-collinear} but ferromagnetically coupled spins), which are embedded in, but either partially or completely isolated from the FM matrix by zones of frustrated spins surrounding the finite clusters. According to this model, the exchange interaction between spins in the FM matrix weakens as $T \rightarrow T_C$ while the FM coupling between the spins within the finite clusters is still quite strong due to the higher Curie temperature for the clusters. As a consequence, the spins of the clusters that are \textit{partially isolated} from, and hence weakly interact with, not only the FM matrix but also the neighbouring clusters (the so-called strongly interacting clusters), can grow in size with temperature through two mechanisms. In one such mechanism, they can merge together because of the strong coupling between the neighboring clusters to form a bigger cluster. In the other mechanism, the cluster spins are able to polarize an increased number of spins originally belonging to the FM matrix via direct exchange interactions, and hence the clusters grow in size at the expense of the spins contained in the FM matrix. However, the temperatures in excess of $T_C$ disorder not only the FM matrix but also the clusters and hence the cluster size decreases for temperatures above $T_C$. On the other hand, so far as the direct exchange interactions are concerned, the clusters which are completely isolated from the FM matrix and also from other clusters (the so-called non-interacting clusters) cannot grow in size with increasing temperature, in agreement with the above observation (vi). The net result of the temperature-induced cluster growth and the existence of many isolated clusters is that a \textit{major} fraction of total spins resides in the \textit{finite} clusters for temperatures in the vicinity of $T_C$. The growth process resulting in an increasing presence of large clusters would naturally enhance long-range RKKY and dipolar interactions among clusters, because of the large magnitude of the cluster moments. Moreover, the observations (i)-(iv) can be explained only\textsuperscript{3,12,20,23,24,28} in terms of the FM cluster-FM matrix model.

If the spins within the clusters (matrix) were antiferromagnetically (ferromagnetically) coupled, as considered in the antiferromagnetic (AF) spin cluster-FM matrix model\textsuperscript{2,4,6,9}, it is not easy for the AF cluster spins to polarize the FM matrix spins and thereby grow in size with increasing temperature because of a much higher energy cost involved in this process. Thus, the above observations do not support such a model.

Furthermore, from a recent spin polarized neutron scattering determination of the structure factor, Wildes et al.\textsuperscript{20} conclude that in direct contradiction with the proposal of Ryan \textit{et al.}\textsuperscript{21,32,33} that FeZr glasses are collinear ferromagnets with strong spin fluctuations for $T_J < T < T_C$, non-collinear spin components are ferromagnetically correlated over several atomic spacings and that the fraction of magnetic moments that are collinear with the mean ferromagnetic direction is small. This observation lends a firm support\textsuperscript{20} to the FM cluster-FM matrix model\textsuperscript{3,12,20,23,24}.

The final picture about the nature and origin of magnetic inhomogeneities in a-Fe\textsubscript{100-x}Zr\textsubscript{x} alloys that emerges from the foregoing discussion is that, due to local atomic density fluctuations, which give rise to spin frustration at the interfaces between the low density pockets and the high density bulk, the spin system consists of an \textit{infinite} three-dimensional \textit{ferromagnetic network (matrix)} and \textit{finite} spin clusters (composed of a set of \textit{non-collinear} but ferromagnetically coupled spins), which are embedded in, but either partially or completely isolated from, the FM matrix by zones of frustrated spins surrounding the finite clusters, as shown in Figure 3.

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SPECIAL SECTION: PHYSICS OF MATERIALS


ACKNOWLEDGEMENTS. I thank all the collaborators within and outside India as well as my research students who have contributed significantly to the work presented here.