Ferromagnetism and spin glass in amorphous Fe–Zr alloys

M. Yu and Y. Kakehashi
Hokkaido Institute of Technology, Maco, Teine-ku, Sapporo 006 (Japan)

H. Tanaka
IBM Research, Tokyo Research Laboratory, IBM Japan Ltd. 1623-14, Shimotsuruma, Yuiato, Kanagawa 242 (Japan)

Abstract

Magnetic properties of the amorphous Fe–Zr alloys have been investigated on the basis of a finite temperature theory of magnetism for amorphous alloys with strong local environment effects. The obtained magnetic phase diagram and magnetization vs. concentration curve explain well those obtained from experimental data, exhibiting a spin-glass ferromagnet transition. It is demonstrated that the spin-glass behaviour near the amorphous pure Fe is mainly caused by the competition between the short-range ferromagnetic interactions and long-range antiferromagnetic interactions via structural disorder, while the formation of ferromagnetism with increasing Zr concentration originates in the band narrowing at the Fe site, which is caused by a reduction in average coordination number of Fe atom due to the difference between Fe and Zr atomic sizes. The re-entrant spin-glass behaviour in Fe-rich amorphous alloys is shown to be realized by the thermal spin fluctuations of amplitude of local magnetic moment.

The magnetic properties in amorphous Fe–Zr alloys have been much investigated in the last decade because of their peculiar behaviours. For example, the magnetization vs. concentration curve deviates from the generalized Slater–Pauling curves beyond 85 at.% Fe [1–3]. The Curie temperatures $T_C$, exhibiting a maximum around 80 at.% Fe, drop sharply beyond 85 at.% Fe, and the spin-glass (SG) state appears after the disappearance of ferromagnetism [1, 4], which suggests the existence of the SG state in the amorphous pure Fe. Furthermore, the re-entrant SG behaviour has been found near the boundary between SG and ferromagnetic states.

In order to understand these magnetic behaviours, and especially their mechanism, we have recently developed a finite temperature theory of magnetism [5], which enables us to perform numerical calculations for amorphous alloys at arbitrary concentration. In this article, we present our numerical results for the magnetic properties of the amorphous Fe–Zr alloys and elucidate their magnetic behaviours on the basis of the new theory.

Before discussing our numerical results, we briefly review our theory. Amorphous transition metal alloys are well known as itinerant electron systems, whose magnetism is dominated by thermal spin fluctuations at finite temperatures and is very sensitive to their electronic structure. Therefore, we adopt the functional integral method which takes into account the thermal spin fluctuations. The method transforms the interacting electron system into a non-interacting electron system with fictitious exchange fields $\xi_j$ acting on each site. The thermal average $\langle m_j \rangle$ of local magnetic moment (LM) on site $j$ is then expressed by a classical average of the field variable $\xi$ on the same site within the static approximation. After making use of a molecular field approximation, we obtain

$$
\langle m_j \rangle = \frac{\int d\xi \xi_j e^{-\beta U(\xi)}}{\int d\xi e^{-\beta U(\xi)}}
$$

(1)

Here $\beta$ denotes inverse temperature.

The energy functional $U(\xi)$ in eqn. (1) consists of the single-site energy $E_j(\xi)$, the atomic pair energy $\Phi_{ij}(\xi)$ between the central site $i$ and the neighbouring site $j$, and the exchange pair energy $\Phi_{ij}(\xi)$ as follows:

$$
U(\xi) = E_j(\xi) + \sum_{i,j} \left[ \Phi_{ij}(\xi) - \Phi_{ij}(\xi) \langle m_j \rangle \right] \frac{\langle m_i \rangle}{\xi_j}
$$

(2)

Here $\langle m_i \rangle$ denotes the amplitude of the LM at the neighbouring site $i$.

The energies at the right-hand side of eqn. (2) are expressed by a one-electron Green's function with
structural and configurational disorders. The calculations are greatly simplified if one adopts the geometric mean model for the nearest-neighbour (NN) interatomic distance \( d \), \( R_{\alpha\beta} = (R_{\alpha\beta}^{-1} + R_{\beta\alpha}^{-1})^{1/2} \). Here \( \alpha(\beta) \) denotes the type of atom on the site \( \langle j \rangle \). After making use of the geometrical mean model and the Bethe-type approximation, the central LM is given by the coordination number \( z \) on the NN shell, the surrounding atomic configuration \( \{ j \} \), the neighbouring LMs \( \langle m_\alpha \rangle \), the square \( |t_{\alpha\beta}|^2 \), of transfer integrals, the effective self-energy \( \epsilon_{\alpha \alpha} \) for electrons with spin \( \alpha \) describing the structural disorder outside the cluster, and the effective medium \( |x_{\alpha\beta}| \) describing the thermal spin fluctuations.

\[
\langle m_\alpha \rangle = \langle m_\alpha \rangle \langle z \rangle \langle \{ j \} \rangle \langle |t_{\alpha\beta}|^2 \rangle \langle |x_{\alpha\beta}| \rangle \langle |x_{\alpha\beta}|^{-1} \rangle
\]

Here \( \{ j \} \) is the type of atom at the neighbouring site \( j \). The above equation shows that the central LM \( \langle m_\alpha \rangle \) is determined by the surrounding LMs \( \langle m_\alpha \rangle \). Therefore, we can obtain self-consistent equations for the average LM \( \langle m_\alpha \rangle \), and the SG order parameter \( \langle |t_{\alpha\beta}|^2 \rangle \). Here \( \langle \{ j \} \rangle \) and \( \langle |t_{\alpha\beta}|^2 \rangle \) denote the structural and configurational average respectively. The effective media \( \epsilon_{\alpha \alpha} \) and \( |x_{\alpha\beta}|^{-1} \) are also obtained self-consistently by assuming the average densities of states (DOSs) for amorphous pure metals.

The self-consistent equations contain the parameters controlling random variables \( z \), \( \{ j \} \) and \( |t_{\alpha\beta}|^2 \). They are given in the present theory by the average coordination number \( z\langle n \rangle \) of \( \alpha \) atom at the NN neighbouring \( \alpha \) atom, and the fluctuations \( \langle 0 | R_{\alpha\beta} | 0 \rangle \) in the NN interatomic distance. It should be noted that \( z\langle n \rangle \) is the average coordination number in the amorphous pure metal \( \alpha \). The probability \( P_{\alpha \beta} \) is given by the atomic short-range order parameter \( \tau_{\alpha \beta} \) \( = P_{\alpha \beta} = e^{\epsilon_{\alpha \beta} - e^{\epsilon_{\alpha \beta}} \tau_{\alpha \beta}} \). It should be noted that \( \tau_{\alpha \beta} \) is the spin-averaged of the sum rule \( z\langle n \rangle \) \( = z\langle n \rangle \) of the \( \alpha \) part. They are determined by the condition of the most random atomic configuration \( \epsilon_{\alpha \beta} \). The input average DOS for the amorphous pure Fe and Zr are obtained from first-principles calculations [7]. The d electron numbers are chosen as \( n_{\alpha\beta} = 7.0(1 - \epsilon_{\alpha\beta}) \times 0.5 \) and \( n_{\beta\alpha} = 3.0 \), because of the large difference of atomic levels between Fe and Zr atoms. It may lead to a change in d electron number \( n_{\alpha\beta} \) with concentration, while the change in the Zr part is neglected because of its small influence on magnetisation. The average coordination numbers \( z\langle n \rangle \) are determined via the following parameters: \( z\langle n \rangle = 7.0 \), \( z\langle n \rangle = 16.0 \) and \( z\langle n \rangle = 11.5 \). Other input parameters are chosen as \( J_{\alpha} = 0.064 \) Ryd, \( J_{\beta} = 0.046 \) Ryd [8] and \( [\delta R_{\alpha\beta}]^2/\langle R_{\alpha\beta} \rangle = 0.06 \) [9], where \( [J_{\alpha}] \) are the effective exchange energy parameters and \( [\delta R_{\alpha\beta}]^2/\langle R_{\alpha\beta} \rangle \) is the fluctuation in the NN interatomic distance \( R \). These input parameters reproduce well the average local DOS obtained from the first-principles calculations by Turek et al. [10].

In Fig. 1, we present our numerical result for the magnetic phase diagram which is obtained from the magnetisation and SG order parameter vs temperature curves. Calculated \( T_C \) exhibit a maximum of 420 K around 70 at.% Fe and then rapidly decrease until the triple point (875 at.% Fe in the present choice of parameters). The SG temperatures \( T_B \) start from 150 K at the triple point and increase to 240 K at pure Fe. These transition temperatures are overestimated by a factor of about 1.5 because of the molecular field approximation. We found the re-entrant SG behaviour near the SG ferromagnetic boundary in Fe-rich amorphous alloys, in agreement with the experimental data of Fukumichi et al. [4]. In the present calculations, we did not obtain the SG behaviour below 50 at.% Fe which was observed experimentally. The SG below 50 at.% Fe may be attributed to the competition between the NN ferromagnetic interactions and the next-NN antiferromagnetic interactions neglected in the present theory.

 reserv

![Graph](image)

**Fig. 1.** Calculated magnetic phase diagram of the amorphous Fe-Zr alloys, showing paramagnetism (P), ferromagnetism (F), SG, and re-entrant SG (RS). The inset shows the experimental result of Fukumichi et al. [4]. Curie temperatures \( T_C \) and SG temperatures \( T_B \) below 50 K are drawn by an extrapolation.
In the SG states beyond 90 at.
Fe, the structural disorder leads to nonlinear magnetic couplings between the NN Fe LMs. They strongly depend on the amplitude of the central Fe LM in the cluster: the central Fe LM ferromagnetically couples with the NN Fe LMs when the amplitude is large, but antiferromagnetically couples with them when the amplitude is small. Thus the nonlinear magnetic couplings bring about the existence of the ferro- and antiferromagnetic NN interactions, because of a broad distribution of the amplitudes of Fe LMs which extends from 0 to 2.4 $\mu_B$. On the contrary, we found rather strong ferromagnetic correlation between the central and the NN Fe LMs (i.e., $\langle (\mu_B^{\text{Fe}})(\mu_B^{\text{NN}}) \rangle > 0.15$ at 75 K), which is favorable for the formation of a ferromagnetic cluster. Furthermore, we found the long-range antiferromagnetic interactions by examining the response of the central Fe LM when the effective medium is polarized. Thus, the SG state is considered to be caused by the competition between the short-range ferromagnetic interactions and long-range antiferromagnetic interactions, as well as the competition between the short-range ferro- and antiferromagnetic interactions.

Near the boundary between the SG and the ferromagnetic states, the magnetic states become very sensitive to the ratio of the short-range ferromagnetic interactions to the long-range antiferromagnetic interactions. The thermal spin fluctuations change these magnetic couplings via the amplitude of the NN Fe LMs and the effective medium which is again dominated by the amplitude of LMs. This leads to a change in the ratio to be more favorable for ferromagnetism when the temperature increases, so that a net magnetization appears at re-entrant SG temperatures. It turns out that the re-entrant SG behavior in Fe-rich amorphous alloys is realized by the thermal spin fluctuations of amplitudes of LMs.

Magnetization vs. concentration curves at 75 K are drawn in Fig. 2. The magnetization exhibits a rapid drop beyond 80 at.
Fe in qualitative agreement with the experimental data which are plotted by open symbols on Fig. 2. The average coordination number $z^{\text{Fe}}_{\text{NN}}$ decreases when the small Fe atoms on the NN shell of an Fe atom are replaced by the large Zr atoms with decreasing Fe concentration. This shrinks the bandwidth and develops the peak near the Fermi level of the Fe local DOS. These changes in the electronic structure with decreasing $z^{\text{Fe}}_{\text{NN}}$ cause the SG-ferromagnet transition with increasing Zr concentration. In fact, we have checked that no magnetization was obtained at 65 at.
Fe at 75 K in the case of the same atomic size ($z^{\text{Fe}}_{\text{NN}} = 9$, $z^{\text{Zr}}_{\text{NN}} = 14$, $r^{\text{Fe}}_{\text{NN}} = -0.26$ and $r^{\text{Zr}}_{\text{NN}} = 0.14$). Recently, Turek et al. [10] have calculated the ground state magnetization as a function of concentration on the basis of the LMTO supercell approach with 64 atoms in a unit cell, assuming the same unit cell for the magnetic and crystalline structures. Their results still hold a finite value even in the amorphous pure Fe (see the full circles in Fig. 2). This is probably attributed to the small number of configurations (64 configurations) and the periodic boundary condition adopted in their self-consistent solutions. The former seems to be insufficient to describe a reasonable phase transition such as the transition from ferromagnetism to the SG, and the latter may lead to an overestimate of ferromagnetism since the magnetic unit cell should be larger than the crystalline unit cell when there is the competition between ferromagnetic and antiferromagnetic interactions in a system. An overestimate of ferromagnetism with use of the same calculation scheme has been found in the Fe-Cr alloys beyond 70 at.
Fe [11], where the theoretical magnetization remains in contradiction to the experimental data revealing the SG states [12]. It should be noted that the present theory reproduces the SG in the Fe-Ni crystalline alloys because of the self-consistent determination of the LMs with use of the distribution function method [13].

In summary, we have investigated the magnetic properties in the amorphous Fe-Zr alloys on the basis
of our new theory. We have clarified that the SG near the amorphous pure Fe is mainly realized by the competition between short-range ferromagnetic and long-range antiferromagnetic interactions via structural disorder. The ferromagnetism is stabilized with increasing Zr concentration by the bond narrowing at the Fe site due to the decrease in average coordination number of Fe atoms caused by the large difference in atomic size between Fe and Zr atoms. The appearance of re-entrant SG behaviour in Fe-rich alloys has been shown to originate in the thermal spin fluctuations of amplitudes of LMs which are characteristic of itinerant magnetism. More details on the other magnetic properties will be published in a separate paper.

Acknowledgments

The authors would like to thank Professor K. Fukamiuchi, Professor N. Kataoka and Dr. A. Fujita for valuable discussions.

References