Theory of magnetism in amorphous Fe–Zr alloys

M. Yu *, Y. Kakehashi

Hokkaido Institute of Technology, Maeda, Teine-ku, Sapporo 006, Japan

Received 12 October 1995; revised 4 March 1996

Abstract

Various magnetic properties of amorphous Fe–Zr alloys have been investigated on the basis of the finite-temperature theory of amorphous magnetic alloys. The numerical results explain the overall features of the magnetization versus concentration curve and the magnetic phase diagram showing the spin glass, the ferromagnetism, and the paramagnetism, including the re-entrant spin-glass behavior in the Fe-rich region. It is verified by various analyses that the spin glass is caused by the nonlinear magnetic couplings and the fluctuations of the amplitudes of local moments due to structural disorder, while the ferromagnetism is stabilized by the decrease in the average coordination number of Fe atoms due to atomic size effects. Broad distributions of the local magnetic moments are found in both spin-glass and ferromagnetic states in the Fe-rich region. Their concentrations and temperature dependences are elucidated on the basis of the electronic structure and nonlinear magnetic couplings. Calculated high-field susceptibilities explain the anomaly around the re-entrant spin-glass region. Calculated effective Bohr magneton numbers predict a minimum around 35 at% Fe. The effects of atomic short-range order on the magnetic phase diagram are also investigated. It is found that the ferromagnetism disappears in the whole concentration when the probability of finding an Fe atom at the neighboring site of an Fe atom is larger than 0.8.

Keywords: Amorphous Fe–Zr alloys; Itinerant magnetism; Spin-glass; Re-entrant spin-glass; Ferromagnetism; Curie temperature; Local environment effects; Atomic short-range order

1. Introduction

The magnetic properties of amorphous Fe–Zr alloys have been extensively investigated from experimental and fundamental points of view [1–10] because of their peculiar behaviors, such as the spin glass (SG) and re-entrant spin-glass (RSG) behaviors in the Fe-rich region. The ground-state magnetization increases steadily from zero at a critical concentration near 38 at% Fe, and shows a maximum around 85 at% Fe. Further increases in the Fe concentration lead to a deviation of the magnetization from the generalized Slater–Pauling curves [3,8]. The Curie temperatures \( T_c \) in the ferromagnetic region rise to a maximum 270 K around 80 at% Fe, and begin to drop sharply beyond 85 at% Fe. It was found from the susceptibility versus temperature curves that the alloys show the RSG behavior near the SG ferromagnetism (F) phase boundary \(( \sim 90 \text{ at}\% \text{ Fe}) [1,4]\). Quite recently, the pure SG state has been found at 93.5 at% Fe [6] with \( T_g = 112 \text{ K} \); this strongly supports the existence of SG in amorphous pure Fe. These properties are common to the Fe-rich amorphous alloys containing early transition metals or rare-earths.
Numerical calculations for the ground-state electronic structure have been done by Krey et al. [8,9] and Turek et al. [10] by making use of the supercell approach, in which the amorphous alloy is simulated by an amorphous compound with a large unit cell. These results have explained the ferromagnetism below 90 at% Fe. But the magnetization remains finite even beyond 93 at% Fe, in contrast to the experimental results [6]. The SG in amorphous pure Fe, on the other hand, has been successfully explained by one of the authors [11] on the basis of the finite-temperature theory of amorphous metallic magnetism. It has been shown that the SG is caused by the nonlinear magnetic couplings between Fe local moments (LMs) and the local environment effects on the amplitude of Fe LMs due to structural disorder.

The present authors have recently extended the theory to amorphous magnetic alloys [12]. The theory drastically simplifies the numerical calculations by means of the geometrical-mean model [13] for the amorphous structure as well as the electronic structure, and allows us to investigate the magnetism in amorphous transition-metal alloys with large differences in atomic size. It has been verified from the numerical calculations that the theory describes quantitatively the spin-polarized local densities of states (DOS) at low temperatures, and describes an overall feature of the magnetic phase diagram for amorphous Fe-Zr alloys: the SG, RSG, F and paramagnetism (P) with decreasing Fe concentration. The SG in the Fe-rich region has been shown to be formed by the same mechanism as found in amorphous Fe, while the ferromagnetism is stabilized by a decrease in the average coordination number of Fe atoms with reducing Fe concentration because of the atomic size effect. The RSG behavior near the SG-F boundary was found to be realized by the thermal spin fluctuations of the amplitudes of Fe LMs, being characteristic of the itinerant electron system.

In the present paper we investigate various magnetic properties of amorphous Fe-Zr alloys in more detail, using the same approach to clarify the following points. First, we clarify the SG-F-P transition by calculating the concentration dependence of various magnetic moments. This verifies the basic mechanism of the phase transition in Fe-rich amorphous alloys containing early transition metals, which was proposed in our previous paper [12]. Second, we investigate the nature of disorder on the LM in amorphous Fe-Zr alloys, calculating the concentration and temperature dependence of the LM distribution. This is useful for the interpretation of the internal field distribution in the Mössbauer experiments [9]. Third, we clarify the anomalies in the high-field spin susceptibilities and the paramagnetic susceptibilities at the critical concentrations and temperatures [7,3,14].

Another problem we discuss in this paper is the effect of atomic short-range order (ASRO). It is well known that the magnetization and transition temperatures in amorphous Fe–Zr alloys are sensitive to the preparation conditions [5,15]. For example, $T_c$ in sputtered Fe–Zr alloys are higher than those in the alloys obtained by the melt-spinning or ion-beam-mixing methods in the Fe-rich region [5]. The magnetization around 50 at% Fe in sputtered samples increases after annealing [15]. These effects must be related to their local atomic structures such as the ASRO or topological short-range order, which change their electronic structures.

In Section 2 we review briefly the finite-temperature theory of amorphous magnetic alloys. In Section 3 we present and discuss our numerical results of calculations for various magnetic properties as functions of concentration and temperature. This section consists of four subsections. In Section 3.1 we present the concentration dependence of the magnetization and various LMs. Their microscopic interpretations are presented on the basis of the electronic structure of amorphous alloys. In Section 3.2 we clarify the distribution of LMs at various concentrations and temperatures. It is shown that there is broad distribution of LMs in both the SG and the ferromagnetic regions, reflecting the large fluctuations of LMs due to configurational and structural disorders. In Section 3.3 we present the high-field spin susceptibilities and the temperature dependence of the spin susceptibility. These results show anomalies at the critical concentrations of the SG–P, SG–F and F–P phase transitions, and verifies the SG–F–P transition in the phase diagram. It is found that the effective Bohr magneton numbers show a minimum of around 35 at% Fe, and diverge toward the pure Zr limit due to the Pauli paramagnetic behavior. In Section 3.4 we investigate the ASRO effects on the magnetization. We show that an increase in the
ASRO parameter of the Fe atom can reduce the magnetization, which may explain the different results obtained under different preparation conditions [5,15]. Finally, in Section 4 we summarize our numerical results.

2. Theoretical framework

We adopt the degenerate-band Hubbard model with Hund's rule coupling to describe the binary amorphous transition metal alloys. Thermal spin fluctuations are taken into account by means of the functional integral method [16-18], which transforms the interacting electron system into a one-electron system with time-dependent fictitious fields acting on each site. Within the static and molecular-field approximations [19-21], the thermal average of LMs on site 0 is given in a classical form as follows [12]:

\[
\langle m_0 \rangle = \frac{\int \text{d} \xi \text{e}^{-\beta \Psi_0(\xi)}}{\int \text{d} \xi \text{e}^{-\beta \Psi_0(\xi)}},
\]

\[
\Psi_0(\xi) = E_0(\xi) + \sum_{j \neq 0} \Phi_{0j}^{(\alpha)}(\xi) - \sum_{j \neq 0} \Phi_{0j}^{(z)}(\xi) \frac{\langle m_j \rangle}{x_j},
\]

where \( \beta \) is the inverse temperature. The field variable \( \xi \) can be regarded as an adiabatic LM on site 0 according to Eq. (1). The energy \( \Psi_0(\xi) \) consists of the single-site energy on site 0 \( E_0(\xi) \), the atomic pair energy between sites 0 and \( j \) \( \Phi_{0j}^{(\alpha)}(\xi) \), and the exchange pair energy \( \Phi_{0j}^{(z)}(\xi) \) between the central LM \( \xi \) and the neighboring LM \( \langle m_j \rangle \) with average amplitude \( x_j \).

In amorphous alloys, the structural and configurational disorders cause a random distribution in both the potentials (diagonal disorder) and the transfer integrals (off-diagonal disorder), which make it difficult to calculate the energies \( E_0(\xi) \), \( \Phi_{0j}^{(\alpha)}(\xi) \), and \( \Phi_{0j}^{(z)}(\xi) \). We consider a cluster consisting of the central atom and its nearest-neighbor (NN) shell, and adopt the geometrical-mean model [13] outside the cluster for the electronic structure calculation. This model simplifies the calculation by transforming the configurational disorder in the off-diagonal term into that of the diagonal term. In this case, the energies in Eq. (2) are calculated from the squares of the NN transfer integrals \( t_{ij}' \) for amorphous pure metals, the effective medium \( \mathcal{E}_\sigma \) for electrons describing the effects of random potentials and thermal spin fluctuations, and the effective self-energy \( \mathcal{S}_\sigma \) describing the structural disorder outside the NN shell (see Ref. [12] for further details).

The central LM \( \langle m_0 \rangle \) is then determined by the coordination number \( z \), the atomic configuration \( \{y_j\} \), the surrounding LM \( \{\langle m_j \rangle\} \), and the squares of the transfer integrals \( \{t_{ij}'\} \), as well as the effective media \( \mathcal{E}_\sigma \) and \( \mathcal{S}_\sigma \):

\[
\langle m_0 \rangle = \langle m_0 \rangle \left\{ z, \{y_j\}, \{\langle m_j \rangle\}, \{t_{ij}'\}, \{\mathcal{E}_\sigma\}, \{\mathcal{S}_\sigma\} \right\}.
\]

The random variables in Eq. (3) are treated by means of the distribution function method; we introduce the distribution functions \( g_\alpha(\langle m_j \rangle) \) for the LMs, the distribution \( p_a(z) \) for coordination number of atom \( \alpha \), the probability \( p^{\alpha\alpha} \) of finding an atom of type \( \alpha \) on the NN site of the central atom \( \alpha \), and the distribution \( p_i(y_j) \) for squares of the transfer integrals. An integral equation for the distribution of LMs is then obtained via Eq. (3) by assuming \( g_\alpha(\langle m_0 \rangle) = g_\alpha(\langle m_j \rangle) \).

After making use of the decoupling approximation, which is correct up to the second moments, we reach the final expression of the self-consistent equations for the average LM \( \langle \langle m_\alpha \rangle \rangle \) of atom \( \alpha \) and the SG order parameter \( \langle \langle m_s \rangle \rangle \) as follows:

\[
\left[ \begin{array}{c}
\langle \langle m_\alpha \rangle \rangle \\
\langle \langle m_\alpha \rangle \rangle^2
\end{array} \right]_c = \int \left[ \begin{array}{c}
M \\
M^2
\end{array} \right] g_\alpha(M) \text{d}M
\]

\[
= \sum_z p_a(z) \sum_{n=0}^z \Gamma(n,z,p^{\alpha\alpha}) \left[ \left[ \langle \langle m_\alpha \rangle \rangle \right]_c \right]_c,
\]

\[
\left[ \left[ \langle \langle m_\alpha \rangle \rangle \right]_{n} \right]_c = \sum_{n=0}^{z-n} \Gamma(i,n,\frac{1}{2}) \sum_{j=0}^{z-n} \Gamma(j,z-n,\frac{1}{2})
\]
\[
X \sum_{k_1=0}^{i} \Gamma(k_1,i,q_\alpha) \sum_{k_2=0}^{n-i} \Gamma(k_2,n-i,q_\alpha) \\
\times \sum_{l_1=0}^{j} \Gamma(l_1,j,q_\alpha) \sum_{l_2=0}^{z-n-j} \Gamma(l_2,z-n-j,q_\alpha) \\
\times \left[ \left\langle \xi_\alpha \right\rangle (z,n,i,j,k_1,k_2,l_1,l_2) \right] \\
\times \left[ \left\langle \xi_\alpha \right\rangle (z,n,i,j,k_1,k_2,l_1,l_2)^2 \right],
\]
(5)
\[
q_\alpha = \frac{1}{2} \left[ 1 + \frac{\langle \langle m_\alpha \rangle \rangle_s}{\langle \langle m_\alpha \rangle \rangle_s^{1/2}} \right],
\]
(6)
where \[ \langle \rangle_s \] denotes the structural (configurational) average. The suffix denotes the type of atom on the central site.

In the self-consistent Eq. (4), we adopt the simplest distribution for \( z \):
\[
p_a(z) = (z^*_a - [z^*_a]) \delta_{z - z^*_a} \\
+ ([z^*_a] + 1 - z^*_a) \delta_{z - z^*_a},
\]
(7)
where \( z^*_a \) is the average coordination number. \( \Gamma(n,z,p) \) in Eq. (4) is the binomial distribution function given by \( \Gamma(n,z,p) = p^n(1 - p)^{z - n}/n!(z - n)! \). The probability \( p_a \) for the atomic configuration \( \gamma \) is described by Cowley’s ASRO parameter \( \tau_a \) and concentration \( c_a \) as
\[
p_a = c_a + (1 - c_a) \tau_a.
\]
The degree of structural disorder via \( \{ t_0 \} \) is described by the fluctuation of the NN interatomic distance \( R \), i.e. \([\langle \delta R \rangle^2 \rangle_s^{1/2} / \langle R \rangle]\).

The thermal average of adiabatic LM \( \xi \) in Eq. (5) is expressed as
\[
\langle \langle \xi_\alpha \rangle \rangle_s(z,n,i,j,k_1,k_2,l_1,l_2) \\
= \int d\xi \xi \exp\left[ -\beta \Psi_a(\xi,z,n,i,j,k_1,k_2,l_1,l_2) \right] \\
\int d\xi \exp\left[ -\beta \Psi_a(\xi,z,n,i,j,k_1,k_2,l_1,l_2) \right],
\]
(9)
where
\[
\Psi_a(\xi,z,n,i,j,k_1,k_2,l_1,l_2) \\
= E_\alpha(\xi,z,i + j) + i \Phi^{(a)}_{a+a}(\xi,z,i + j) \\
+ (n - i) \Phi^{(a)}_{a+a}(\xi,z,i + j) \\
+ j \Phi^{(a)}_{a+a}(\xi,z,i + j) \\
+ (z - n - j) \Phi^{(a)}_{a+a}(\xi,z,i + j) \\
- [(2k_1 - i) \Phi^{(a)}_{a+a}(\xi,z,i + j) \\
+ (2k_2 - n + i) \Phi^{(a)}_{a+a}(\xi,z,i + j)] \\
\times \left[ \left[ \langle \langle m_\alpha \rangle \rangle_s \right]_s^{1/2} \right],
\]
(10)
In Eq. (10), the subscripts + and - denote the contracted \( ([R] - [\langle \delta R \rangle^2]_s^{1/2}) \) and stretched \( ([R] + [\langle \delta R \rangle^2]_s^{1/2}) \) pairs for interatomic distances, respectively.

In the present method, the structural disorder in the transfer integrals \( \{ t_0 \} \) in a cluster is described by the number \( i \) (\( j \)) of contracted atoms \( \alpha \) (\( \bar{\alpha} \)) among \( n \) (\( z - n \)) atoms of type \( \alpha \) (\( \bar{\alpha} \)) on the NN shell, and the spin configuration is described by the number \( k_1 \) of up-spins among the \( i \) (\( j \)) contracted atoms \( \alpha \) (\( \bar{\alpha} \)) and the number \( k_2 \) (\( l_2 \)) of up spins among the \( n - i \) (\( z - n - j \)) stretched atoms \( \alpha \) (\( \bar{\alpha} \)). The effective media \( \mathcal{Z}_\alpha \) and \( \mathcal{S}_\sigma \) are obtained by solving the self-consistent coherent-potential approximation (CPA) and Bethe-type equations (see Eqs. (49) and (82) in Ref. [12]), in which we need the average DOS for amorphous pure metals as an input.

The atomic size effect is taken into account via average coordination number \( z^*_a \), which is given by
\[
z^*_a = z^*_a(0) + p^{\alpha\alpha}[z^*_a(1) - z^*_a(0)],
\]
(11) where the average coordination numbers \( z^*_a(0) \) and \( z^*_a(1) \) are the values for \( p^{\alpha\alpha} = 0 \) and \( p^{\alpha\alpha} = 1 \), respectively, which are estimated approximately from the dense random packing of hard spheres (DRPHS) model (see Appendix B in Ref. [12]). This relation means that the coordination number of atom with larger atomic size increases linearly with decreasing the same type of neighboring atoms. Moreover, it should be noted that the atomic size effect causes \( \tau_a \neq \tau_{\bar{a}} \) because of the sum rule \( z^*_a(1 - \tau_a) = z^*_a(1 - \tau_{\bar{a}}) \) for the \( \alpha - \bar{\alpha} \) pair. We determine these pa-
parameters from the condition of the most random atomic configuration (see Appendix A in Ref. [12]).
\[ c_\alpha \tau_\alpha + c_\beta \tau_\beta = 0 \]  
(12)

The present approach allows us to perform qualitatively or semi-quantitatively the numerical calculations for the electronic structure and magnetic properties of amorphous magnetic alloys by solving the self-consistent Eq. (4), as well as the equations for effective media \( \mathcal{Y}_\alpha \) and \( \mathcal{Y}_\beta \).

3. Numerical results

In the numerical calculations, we adopted the input DOS for amorphous Fe and Zr which were calculated by using a tight-binding LMTO (linear muffin-tin orbital) recursion method [22] (see Fig. 1 in Ref. [12]). The d electron numbers are chosen as \( n_{Fe} = 7.0 + (1.0 - c_{Fe})0.5 \), and \( n_{Zr} = 3.0 \). The choice of d electron numbers has been discussed in Ref. [12] (it is based on our first-principles calculations). The effective exchange energy parameters for Fe and Zr are assumed to be \( J_{Fe} = 0.064 \) Ryd and \( J_{Zr} = 0.046 \) Ryd, respectively. The former gives the ground-state magnetization \( 2.3 \mu_B \) for the bcc Fe, and the latter is taken from Janak’s calculation [23]. The fluctuation of interatomic distance \( ((\delta R)^2)^{1/2}/\langle R \rangle \) is chosen to be 0.06, which was estimated from the pair distribution function for amorphous Fe [24,25]. The ASRO parameters \( \{\alpha\} \) are determined from the most random atomic configuration (see Eq. (12)), and the large difference in atomic size between Fe and Zr atoms is taken into account via Eq. (11) with \( z_{Fe}(0) = 7.0 \), \( z_{Zr}(0) = 16.0 \), and \( z_{Fe}(1) = z_{Zr}(1) = 11.5 \). The values of \( \{\tau_\alpha\} \) and \( \{\alpha\} \) are shown in Fig. 2 in Ref. [12]. These parameters reproduce the spin-polarized local DOS for amorphous Fe–Zr alloys calculated from the first-principles calculations [10] and give a reasonable magnetic phase diagram (see Figs. 3 and 4 in Ref. [12]).

3.1. Magnetization

We have calculated the magnetization \( \langle |m| \rangle \) in the most random atomic configuration using the parameters mentioned above. As can be seen from Fig. 1, the magnetization appears at 87.5 at% Fe and shows a maximum of 0.9 \( \mu_B \) at around 75 at% Fe. The result is consistent with the experimental data shown by the circles [2], squares [3], and triangles [8], although the data are considerably scattered in the Fe-rich region. The large difference in magnetization between the experimental and calculated results beyond 80 at% Fe is partly related to the ambiguity of extrapolating the magnetization versus external field curve to the zero field because of the field-dependent slope in the data, and is partly related to the difference in temperature. Note that our results are calculated at 75 K, while the experimental data are obtained at 4.2 K. The magnetization at 0 K becomes larger than that at 75 K by about 0.05 \( \mu_B \) around 80 at% Fe according to an extrapolation of the calculated magnetization versus temperature curve.

The appearance of magnetization is explained by the large difference in atomic size between Fe and Zr atoms, as discussed in our previous paper [12]. In fact, with decreasing Fe concentration, smaller Fe atoms on the NN shell of Fe atom are replaced by larger Zr atoms. This leads to a decrease in the average coordination number \( z_{Fe} \) according to the DRPHS model (see Fig. 2 in Ref. [12]), and therefore causes additional band narrowing as well as the enhancement of the Fe local DOS near the Fermi
level. Below 65 at% Fe, the magnetization decreases linearly and disappears near 28 at% Fe because of the hybridization between Fe 3d and Zr 4d orbitals.

As shown in Fig. 2, the magnetization is dominated by the Fe LM $[(m_{Fe})_{c}]$. The small Zr LM $[(m_{Zr})_{c}]$ is antiparallel to the magnetization since the down-spin electrons on the Zr sites hybridize more with the 3d electrons so that the number of the 4d states for down-spin electrons below the Fermi level becomes larger than that for up-spin electrons. The large deviation of $[(m_{Fe})^{2}]_{c}/2$ from $[(m_{Fe})^{2}]_{c}$ in the Fe-rich region implies that the Fe LMs show large fluctuations due to structural and configurational disorders. The SG order parameter $[(m_{Fe})^{2}]_{c}$ increases toward amorphous pure Fe after the complete disappearance of the magnetization. This is because the amplitudes $[(m_{Fe})^{2}]_{c}/2$ increase with the reduction of hybridization between Fe 3d and Zr 4d orbitals.

The local environment effects on the LM are presented in Fig. 3. It is seen that the Fe LMs increase with increasing number of Fe atoms ($n$) on the NN shell in the Zr-rich region, but they start to decrease when $n$ becomes larger than 8 in the Fe-rich region. In particular, Fe LM with more than 10 Fe NN become antiparallel to the magnetization, although they are not well defined due to the strong structural disorder, as will be shown in the next subsection. These behaviors can be understood from their electronic structure. As shown in Fig. 4, the Fe local DOS with no Fe atom on the NN shell show

![Fig. 2](image2.png)

Fig. 2. Concentration dependence of various local moments in the most random atomic configuration at 75 K: $[(m_{Fe})_{c}]$ (solid curve), $[(m_{Zr})_{c}]$ (dashed curve), $[(m_{Fe})^{2}]_{c}/2$ (dot-dash curve), and $[(m_{Zr})^{2}]_{c}/2$ (dotted curve).

![Fig. 3](image3.png)

Fig. 3. Concentration dependence of LM $[(m_{Fe})_{c}]$ for atom $\alpha$ ($\alpha = Fe$, solid curves; $\alpha = Zr$, dashed curves) with various numbers of $\alpha$ atoms ($n$) on the NN shell, which are defined by $\Sigma_{\alpha} p_{\alpha}(z [(m_{\alpha})_{c}]_{c})$.

![Fig. 4](image4.png)

Fig. 4. Local DOS $[(p_{\alpha}(\omega))_{c}]$ for atom $\alpha$ ($\alpha = Fe$: solid curves, $\alpha = Zr$: dashed curves) with various numbers ($n$) of $\alpha$ atoms on the NN shell in the nonmagnetic amorphous Fe$_{65}$Zr$_{35}$ alloy. The coordination numbers are fixed to be $z_{Fe} = 9$ and $z_{Zr} = 14$. 

\[\text{Fig. 2. Concentration dependence of various local moments in the most random atomic configuration at 75 K:} \]

\[\begin{align*}
[&] & (m_{Fe})_{c} & (m_{Zr})_{c} & (m_{Fe})^{2} & (m_{Zr})^{2} \\
0 & 1 & 0 & 1 & 0 & 0 \\
0.1 & 0.9 & 0.2 & 0.8 & 0.6 & 0.4 \\
0.2 & 0.8 & 0.5 & 0.7 & 0.7 & 0.6 \\
0.3 & 0.7 & 0.6 & 0.8 & 0.8 & 0.7 \\
0.4 & 0.6 & 0.5 & 0.9 & 0.9 & 0.8 \\
0.5 & 0.5 & 0.4 & 1 & 1 & 0.9 \\
0.6 & 0.4 & 0.3 & 1 & 1 & 0.8 \\
0.7 & 0.3 & 0.2 & 1 & 1 & 0.7 \\
0.8 & 0.2 & 0.1 & 1 & 1 & 0.6 \\
0.9 & 0.1 & 0 & 1 & 1 & 0.5 \\
1 & 0 & 0 & 0 & 0 & 0
\end{align*}\]
the Lorentzian form due to the hybridization between the 3d electrons on the central site and the 4d electrons on the surrounding sites. With increasing Fe atoms (n) on the NN shell, the two-peak structure develops in the DOS (see the DOS with n = 4 and 8 in Fig. 4). This enhances the Fe DOS at the Fermi level, therefore leads to larger Fe LM. The high-energy peak, however, shifts above the Fermi level when n goes beyond 9. This suppresses the stability of ferromagnetism and makes the ferromagnetic couplings unstable, leading to the reversal of the Fe LM.

On the other hand, the negative LMs on the Zr sites decrease in magnitude with increasing Zr atoms on the NN shell. As explained above, the negative LMs on the Zr sites are caused by the 3d–4d hybridization. Therefore the magnitude of $\langle m_{zz} \rangle_n$ may be in proportion to the degree of the hybridization or the number of surrounding Fe atoms. This explains the simple n dependence of the Zr LMs.

### 3.2. Distribution of local moments

Calculated distribution functions $g(M) = \sum_n c_n g_n(M)$ in various concentrations at 75 K are presented in Fig. 5. In contrast to the strong ferromagnets such as amorphous Co–Y alloys [26], the distribution functions of LMs in amorphous Fe–Zr alloys show a very broad peak in the range of $0.5 \leq c_{Fe} \leq 0.75$, indicating the large amplitude fluctuations of LM. This explains the broad distribution of hyperfine fields in the Fe-rich region found in the Mössbauer measurements [9].

It is seen from the numerical results in Fig. 5 that the negative Fe LMs appear beyond 75 at% Fe. The broad peak at the positive side flattens and the distribution extends to the negative region with increasing Fe concentration. This is due to the appearance of the nonlinear magnetic couplings between the Fe LMs, which causes competition between ferromagnetic and antiferromagnetic interactions. Such a competition leads to the SG states beyond 90 at% Fe [12].

We note that even the LMs with a given local atomic configuration on the NN shell show a distribution due to the structural disorder as well as the configurational disorder outside the NN atoms. This feature is shown in Fig. 6. The distributions of Fe LMs with 0–4 Fe atoms on the NN shell have small
widths, showing the Fe LMs well defined by their local atomic configuration \( (n) \). This is because the amplitudes of Fe LMs change monotonically with the degree of hybridization between the Fe 3d and Zr 4d orbitals, which fluctuates due to the structural disorder. However, the Fe LMs with more than 8 Fe NN show a very broad distribution because of the nonlinear magnetic couplings between Fe LMs, and the amplitude fluctuations of Fe LMs due to structural disorder.

We have compared our results with those calculated from the supercell approach \[10\]. Reasonable agreement is found in both magnetization and distribution functions of LMs below 80 at% Fe (see the crosses in Fig. 1 and the insets in Fig. 5). The difference is found beyond 90 at% Fe; our results show there the SG, while the results based on the supercell method still show the ferromagnetism. The same kind of difference has been found in the spin-polarized local DOS as shown in Fig. 3 of Ref. \[12\].

As we discussed in our previous paper \[12\], the difference beyond 90 at% Fe may be related to the small number of atoms (64) in a unit cell in the supercell approach and the periodic boundary condi-

![Fig. 7. Distribution functions \( g(M) \) at various temperatures in amorphous Fe\(_{75}\)Zr\(_{25}\) alloy. Note that the SG transition temperature and the Curie temperature are 58 and 154 K, respectively.](image)

![Fig. 8. Distribution functions \( g(M) \) at various temperatures in amorphous Fe\(_{75}\)Zr\(_{25}\) alloy.](image)

The temperature variations of the LM distributions are presented in Fig. 7 for the RSG and in Fig. 8 for the ferromagnetic state. In the RSG region, a small asymmetry corresponding to the appearance of net magnetization is found when the temperature increases. With further increases in temperature, the distribution becomes narrower and finally forms a delta function above \( T_C \). In the ferromagnetic region, on the other hand, the width of distribution first increases, and shows a maximum around 0.5 \( T_C \). It should be noted that the broad distribution remains

![Distribution Functions of Local Moments](image)
3.3. Susceptibility and phase diagram

We have calculated the high-field susceptibilities ($\chi_{HF}$) at 75 K, which are shown in Fig. 9, to investigate the SG–F–P transition with decreasing Fe concentration in more detail. The susceptibility $\chi_{HF}$ is obtained by applying the magnetic field from $5 \times 10^{-5}$ to $5 \times 10^{-4}$ Ryd in units of $g_e \mu_B$, where $g_e = 2.002$, and by taking the numerical derivative of magnetization with respect to the magnetic field. The high-field susceptibilities show asymmetric divergences at both 87.5 and 28 at% Fe, which correspond to the SG–F and F–P phase transitions, respectively. The large $\chi_{HF}$ beyond 87.5 at% Fe is attributed to the directional changes of the LMs due to the applied magnetic field. Although the experimental data are scattered in the Fe-rich region due to different preparation conditions, they are comparable with the calculated ones, and show a rapid increase near the SG–F phase transition (~ 92 at% Fe).

Fig. 10 shows the magnetization and paramagnetic inverse susceptibilities as functions of temperature at various concentrations. The magnetization versus temperature curves show the second-order transition at $T_C$. Note that the calculated transition temperatures are overestimated by a factor of 1.5–2.0. Such overestimates are mainly attributed to the molecular-field approximation used in the present theory [29]. Moreover, the magnetization versus temperature curves show a large deviation from the Brillouin curve at around 80 at% Fe, explaining the Invar behavior in this region [7].

The inverse susceptibilities in the Fe-rich region follow the Curie–Weiss law at high temperatures, while the susceptibilities near amorphous Zr show Pauli paramagnetic behavior. The effective Bohr magneton numbers $m_{eff}$ are obtained from the slopes of the paramagnetic inverse susceptibilities, and are presented in Fig. 11 as a function of concentration. They show a minimum at around 35 at% Fe and increase toward both pure limits (3.4 $\mu_B$ at pure Fe, and 5.2 $\mu_B$ at pure Zr). The large enhancement of $m_{eff}$ near amorphous pure Zr should be attributed to the change from the weak magnetic behavior to the Pauli paramagnetic behavior in this region. Although there are no experimental data for amorphous Fe–Zr alloys to support our results, the values in the liquid Fe (3.9 $\mu_B$ [30]) and in bcc Zr near the melting point...
Fig. 11. Calculated effective Bohr magneton numbers $m_{\text{eff}}$ around 1000 K. • experimental data for liquid Fe [30]. ○ for bcc Zr at 1854 K [28].

(3.5 $\mu_B$ at 1854 K [28]) are in qualitative agreement with our results.

The present theory describes the SG behavior in the Fe-rich region, as shown in Fig. 12(a); the SG order parameter increases below $T_g$, the susceptibility shows a cusp around $T_g$, which is characteristic of the SG and is observed in amorphous Fe$_{93.5}$Zr$_{6.5}$ alloy [6]. The inverse susceptibility shows an upwards convexity above the transition temperature. Such behavior was observed experimentally by Fukamichi [31], but it is considered to be common to the close-packed structure in Fe-rich alloys, since the same behavior is also found in the numerical results for amorphous Fe [29] and fcc Fe [32].

We find the RSG behavior near the 87.3 at% Fe (see Fig. 12b); the magnetization decreases below 70 K and vanishes at 57 K. This is attributed mainly to the large amplitude fluctuations of Fe LMs with increasing temperature. The SG order parameter (dot-dash curve) in Fig. 12, on the other hand, increases with decreasing temperature. The susceptibility obtained in this region diverges at both $T_C$ and $T_g$. These behaviors are consistent with the experimental data in the RSG region [4].

From the temperature dependence of magnetizations and susceptibilities, we obtained the magnetic phase diagram (see Fig. 13). It shows that the numerical results obtained from the most random atomic configuration explain well the SG, F, and P on the $T$--$c$ plane. Note that we found the SG solution even in the concentrated region, but the ferromagnetism is more stable there because of the atomic size effect mentioned in Ref. [12]. As we described in our previous paper [12], the formation of SG in amorphous Fe--Zr alloys is attributed to the nonlinear

Fig. 12. Temperature dependence of the magnetization (solid curve), the SG order parameter (dot-dash curves), and spin susceptibility (solid curves) in (a) amorphous Fe$_{90}$Zr$_{10}$ alloy, and (b) Fe$_{87.3}$Zr$_{12.7}$ alloy. The dotted lines denote the critical temperatures.

Fig. 13. Calculated magnetic phase diagram of amorphous Fe--Zr alloys showing the paramagnetism (P), ferromagnetism (F), spin glass (SG), and re-entrant spin glass (RSG). The SG transition temperatures ($T_g$) below 87.5 at% Fe are denoted by the dotted curve. The phase boundaries below 50 K are extrapolated by dashed lines. Inset: experimental results [6,7], in which the most recent data for 93.5 at% Fe have been added.
magnetic couplings between the NN Fe LMs, and the broad distribution of the amplitudes of LMs \( \langle \xi^2 \rangle^{1/2} \) whose width reaches about 2.4 \( \mu_B \), as seen from Fig. 14. The monotonic increase in \( T_g \) with increasing Fe concentration is caused by the enhancement of the ferro- and antiferromagnetic couplings due to the development of the amplitudes of the Fe LMs.

3.4. Atomic short-range order effects

So far, we have explained various magnetic properties of amorphous Fe–Zr alloys assuming the most random atomic configurations. We examine here how the magnetism is sensitive to the ASRO, calculating the magnetization and the SG order parameter as a function of the ASRO parameters \( \tau_{Fe} \). We found that the magnetization generally decreases with increasing \( \tau_{Fe} \). For example, an increase in \( \tau_{Fe} \) by 0.26 at 75 K around 65 at% Fe leads to a reduction in the magnetization by 0.17 \( \mu_B \). A phase transition from the F to the SG occurs when \( \tau_{Fe} \approx 0.4 \) at the same concentration. This is caused by the band broadening in Fe local DOS and the enhancement of antiferromagnetic couplings as \( z_{Fe} \) increases via \( \tau_{Fe} \) (see Eqs. (8) and (11)).

The calculated phase diagram on the \( p_{FeFe}-c_{Fe} \) plane is presented in Fig. 15. We found the SG when \( p_{FeFe} \gtrsim 0.8 \), the F when \( p_{FeFe} \lesssim 0.8 \) in the Fe-rich region, and the P in the Zr-rich region. It turns out that the ferromagnetism in the Fe-rich region becomes unstable as \( p_{FeFe} \) increases from the most random atomic configuration, and the SG occurs when \( p_{FeFe} \gtrsim 0.8 \). Experimentally, the Curie temperatures \( T_C \) in the sputtered Fe–Zr amorphous alloys are larger than those in the melt-spun or ion-beam-mixed samples [5]. This result seems to be explained by \( p_{FeFe} \) (sputtered) \(< p_{FeFe} \) (melt-spun) or \( p_{FeFe} \) (ion-beam-mixed) according to our phase diagram.

There is no experimental analysis about the difference in ASRO parameter between the samples obtained from different preparations, as far as we know. The experimental data for the local structure obtained from the partial pair distribution functions and Mössbauer spectroscopy are required to understand clearly the problem of structure versus magnetism in amorphous alloys.

4. Summary

We have investigated various magnetic properties of amorphous Fe–Zr alloys on the basis of the
finite-temperature theory of amorphous magnetic alloys. The magnetic phase diagram showing the SG–F–P transition, the concentration dependence of the magnetization and the high-field susceptibilities have been explained by assuming the most random atomic configuration. We have verified a cusp in the susceptibility near $T_g$ in the SG region and the divergences at $T_C$ and $T_g$ in the RSG region, calculating the temperature dependence of the susceptibilities in the Fe-rich region. The SG is caused by the nonlinear magnetic couplings between Fe LMs and the local environment effects on the amplitudes of LMs due to structural disorder. The RSG behavior, however, is realized by the thermal fluctuations in the amplitudes of LMs which unbalance the competition between ferromagnetic and antiferromagnetic couplings.

The magnetization in amorphous Fe–Zr alloys appears below 90 at% Fe and shows a maximum around 80 at% Fe. The appearance of ferromagnetism originates in the decrease in average coordination number $z_{\text{Fe}}$ due to large difference in atomic sizes between Fe and Zr atoms. The monotonic reduction of magnetization below 65 at% Fe, on the other hand, was explained by the hybridization between 3d Fe and 4d Zr orbitals. The SG in the Zr-rich region was not explained by the present calculations. Probably, the magnetic couplings between the distant LMs play an important role in this problem.

The distribution of LMs has been shown to be very broad in both the ferromagnetic and SG states, being consistent with the Mössbauer measurements for hyperfine fields in the Fe-rich region [9]. This behavior is attributed to both the structural and configurational disorders, which lead to the large fluctuations of LMs in direction and amplitude via nonlinear magnetic couplings and the fluctuations in the local band width.

The high-field susceptibilities $\chi_{\text{HF}}$ diverge at the critical concentrations of the SG–F and F–P transitions. We have obtained huge susceptibilities around the critical concentrations, which are comparable to the experimental data. They are attributed to the large change in directions of LMs with respect to the external field.

The paramagnetic inverse susceptibilities follow the Curie–Weiss law at high temperatures. The effective Bohr magneton numbers obtained from the paramagnetic inverse susceptibilities show a minimum around 35 at% Fe and increase towards both pure limits. The latter is due to the weak magnetism in amorphous Fe and the Pauli paramagnetic behavior in amorphous Zr, respectively.

We have shown that the ASRO drastically changes the magnetism of amorphous Fe–Zr alloys. We found that a F–SG transition occurs at $p_{\text{FeFe}}^{\text{F-SG}} \approx 0.8$ in the Fe-rich region because of the band broadening of the Fe local DOS and the strong nonlinear magnetic couplings. We suggest that the different $T_C$ in the sputtered and the melt-spun Fe–Zr alloys can be explained by the different ASROs: $p_{\text{FeFe}}^{\text{sputtered}} < p_{\text{FeFe}}^{\text{melt-spun}}$.

Another factor that changes the local atomic structure is the degree of structural disorder. We have recently proposed a theory which interpolates between crystals and amorphous metals, and have investigated the effect of degree of structural disorder on the magnetic properties of amorphous pure Fe [33]. We found a significant change in the magnetic phase diagram of Fe with a small change of degree in the structural disorder. Such an effect is also expected to be important in amorphous alloys, especially in Fe-rich amorphous alloys. It is highly desired to develop a theory which interpolates between compounds and amorphous alloys to examine the effect.

Finally, we discuss the effect of transverse components of LM, which is neglected in the present calculations. This effect is important for realistic calculations of the magnetic structure. Therefore, we have recently extended our theory to take into account the transverse spin fluctuations [34]. The extended theory tells us the following. First, the expressions of the amplitude of the LM ($\langle m^2 \rangle$; see Eq. (3.20) in Ref. [20]) and local charge fluctuations ($\langle n^2 \rangle$; see Eq. (3.19) in Ref. [20]) are unchanged, so that these quantities are described essentially by the present theory. Second, the transition temperatures ($T_C$ and $T_g$) in the extended theory are reduced by a factor of two because of an overestimate of the magnetic entropy due to the classical treatment of transverse degrees of freedom in the theory. The third point is that the self-consistent equations for $z$ component in the extended theory reduce to Eqs. (4)–(6) in the present theory when we take the most probable configuration for $x$ and $y$ components.
Therefore, we believe that the present theory gives us reasonable results for the quantities related to the z component and the amplitude of LM. This feature is also seen in the recent calculations by Krey et al. [35] and Lorenz et al. [36], where the magnetizations obtained in the collinear calculations agree well with the noncollinear ones in spite of the strong quenching of orbital moments [37].

Acknowledgements

The authors would like to thank Professor K. Fukamichi and Professor K.V. Rao for valuable discussions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture in Japan.

References