Two-cluster Model for Amorphous Fe-Cr-Zr Alloys

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Mossbauer spectra and magnetization at different temperature and on hydrogenation for a series of Fe-Cr-Zr alloys are studied. The bimodal hyperfine field distributions are obtained by the fitting of Mossbauer spectra. Based on the hyperfine field distribution and the improved Langevin function, magnetization curves are fitted. Based on the located energy minimum of two single domain particles, hysteresis loop and spin-glass-like behavior can be explained. All of these experimental and theoretical results prove the existence of two-cluster.

Key words: Mossbauer spectrum, magnetization, amorphous, hyperfine parameter, cluster

1. Introduction

During recent years, amorphous Fe-TM-Zr (TM=3d transition metal) alloys have attracted considerable scientific attention because these alloys exhibit many of interesting physical properties, such as spin-glass-like behavior, Invar effect and resistivity minima¹⁻⁵⁾. To explain these unusual magnetic behaviors, several models have been considered, where the cluster spin-glass model is interesting⁴⁾. The basic idea behind the above models is the existence of competing (ferromagnetic and antiferromagnetic) exchange interactions or two-cluster. In this paper, the two-cluster spin-glass model for amorphous Fe_{90-y}Cr_yZr₁₀ alloys is studied.

2. Experiment

Amorphous Fe_{90-y}Cr_yZr₁₀ (y=0, 4, 7, 13, 16) alloys (hereafter for convenience, B_y is used to denote the as-quenched alloy with Cr content = y) about 1mm wide and 20-30 μm thick supplied by Institute of Physics, Academia Sinica, were prepared by the melt-spinning technique in an argon atmosphere. Amorphousness of the ribbons was checked by x-ray diffraction and Mossbauer spectrum. Mossbauer spectra were obtained in the transmission geometry at temperature ranging from 77K to 300K using a conventional constant-acceleration spectrometer. Typically, 10⁵ counts were accumulated in each channel. The magnetization curves were measured with an extracting sample magnetometer. The measurement accuracy of the magnetic moment is 3×10⁻⁴emu.

3. Results and discussion

3.1 Mossbauer spectroscopy

The typical Mossbauer spectra of series of B_y alloys at room temperature (RT) and 77K are shown in Figs. 1 (a)-(b)³⁾. The Mossbauer spectra of B_y alloys at RT seen in

Fig. 1(a) can be found to be composed of a series of splitting and dissymmetrical superparamagnetic spectra. The existence of superparamagnetic state has been found in a-

Fig. 1 Mossbauer spectra of Fe₉₀Zr₁₀ (a) at RT; (b) at 77K.

Fig. 2 Hyperfine field distributions $P(H_{hf})$ of Fe_{90-y}Cr_yZr₁₀ (y=0, 4, 7, 13, 16) alloys at 77K.

Fe₉₀Zr₁₀ and Fe₉₂Zr₈ alloys⁶⁾. In order to get the best fitting, many fitting ways were tried. Finally, it is found that Mossbauer spectra consist of two sets of quadrupole ones corresponding to S₁ and S₂ sites of Fe atoms are the best for B_y (y=0, 4, 7, 13, 16) alloys. In terms of the computed results, the hyperfine parameters of S₁ and S₂ sites are obtained as follow: the isomer shift of S₂ site $\delta_{IS2} = -0.17 - (-0.29) \times 10^{-3}$ m/s, the quadrupole split $\Delta_2 \approx 0.32 \times 10^{-3}$ m/s; $\delta_{IS1} = -0.00 - (-0.10) \times 10^{-3}$ m/s and $\Delta_1 \approx 0.40 \times 10^{-3}$ m/s; and the values of δ_{IS2} and δ_{IS1} decrease linearly with increasing Cr content. The parameters are near those for B and D sites as measured by Michaelsen et al.⁷⁾ But, at 77K, Mossbauer spectra of B_y (y=0, 4, 7, 13, 16) alloys become ferromagnetic ones, as seen in Fig. 1(b). Figures 2 shows the $P(H_{hf})$ - H_{hf} curves of B_y (y=0, 4, 7, 13, 16) at 77K³⁾. Recently, Kall and co-workers fit Mossbauer spectra of a-Fe₉₀Zr₁₀ alloy at different temperature with the best two-Gaussian and Window method, and obtained the two-Gaussian $P(H_{hf})$ -

H_{hf} curves²⁾ which confirmed the existence of bimodal $P(H_{hf})$ distributions and two-cluster that was also proved in the other Fe-Zr based alloys by the other experiments⁸⁾ Here, the Mossbauer spectra were fit with the improved Hesse method. The $P(H_{hf})$ curves are fit with the best two-Gaussian or three-Gaussian. It is found that the bimodal $P(H_{hf})$ - H_{hf} curves exist mostly in the B_y ($y=0, 4, 7, 13, 16$) alloys. These results prove the existence of two-cluster structure in a-Fe-Cr-Zr alloys.

3.2 Magnetization

Recently, the magnetization curves of a-Fe_{100-x}Zr_x alloys were modeled assuming an ensemble of superparamagnetic particles with a distribution of cluster volume⁴⁾. In order to fit the fact that the magnetization versus magnetic field curve shows no saturation even up to 20T, the large high-field susceptibility term ($\chi_{hf} H$) was introduced artificially. In the study of giant magneto-resistance of heterogeneous alloys films⁹⁾, assuming the same model as in Ref.4, the magnetization is described as follow: $M = pM_s \sum_D f(D) [\coth(mH / (K_B T)) - (K_B T / (mH))]$,

where $m = (M_s / 6)\pi(D^3) = M_s V$, $f(D)$ is the log-normal function, $V(D)$ is the volume (diameter) of superparamagnetic particle, p is the concentration of the ferromagnetic material in the film. Here, we use the same model as in Refs.4 and 9. But, because the moment of superpara-magnetic particle is proportional to the hyperfine field, $m = M_s V = kH_{hf}$, $f(D)$ can be replaced by the hyperfine field distribution $P(H_{hf})$. In addition, the contribution from the low field part of $P(H_{hf})$ curve may give rise to the large high-field susceptibility term. Therefore, the artificial ($\chi_{hf} H$) term has been given up. In the mean-field approximation, we can get the magnetization as follow:

$$\begin{aligned} M(m, H) / M_s &= \int P(m) \left(\coth\left(\frac{m(H + \lambda M)}{K_B T}\right) - \frac{K_B T}{m(H + \lambda M)} \right) dm \\ &= \int P(H_{hf}) [\coth(aH_{hf} H + b) - 1 / (aH_{hf} H + b)] dH_{hf} \end{aligned} \quad (1)$$

where $a=k/(K_B T)$, $b=\lambda m M / (K_B T)$, k is a constant, b is a dimensionless parameter for the interaction. In the fitting of the measured $M(H, T)$ curves, the value of the parameter b can be modified. Using the experimental $P(H_{hf})$ distribution and Eq.(1), we can fit the measured $M(H, T)$ curves by adjusting the values of the parameters a and b . Figure 3 shows the calculated and experimental magnetization curves for a-Fe₉₀Zr₁₀ alloy at 4.2K, 77K and 200K. The experimental $P(H_{hf})$ distribution of a-Fe₉₀Zr₁₀ alloy at 4.2K is taken from Ref.2. The more details of the fitting of the measured $M(H, T)$ curves for a-Fe_{90-y}Cr_yZr₁₀ will be published elsewhere. The calculated and experimental results indicate as follows: (1) The contributionsof bimodal $P(H_{hf})$ distribution to the magnetization curve can be divided into two parts. The high-field Gaussian peak in bimodal $P(H_{hf})$ distribution will give rise to the magnetization curve which is saturated easily. However, the low or little-field Gaussian peak will

Fig.3 The calculated and experimental magnetization curves for of a-Fe₉₀Zr₁₀ alloy. (a)at 4.2K, $a=1$, $b=0$; (b)at 4.2K, $a=1$, $b=4.5$; (c) at 77K, $a=0.5$, $b=0$; (d)at 77K, $a=0.5$, $b=2.0$; (e)at 200K, $a=0.21$, $b=0$; (f)at 200K, $a=0.21$, $b=1.65$.

lead to the magnetization curve which is saturated hard. Therefore, by introducing the $P(H_{hf})$ distribution can we not only describe objectively the distribution of the volume of superparamagnetic particle, but also bring to light the original of the large high-field susceptibility. (2) Comparing the interaction case ($b \neq 0$) with the non-interacting case, we find that the introduction of an interaction (molecular field constant λ or parameter b) has a relatively high effect on the initial susceptibility but it affects only slightly the magnetization curves at higher fields. (3) The experimental and theoretical studies of the magnetization curves for a-Fe_{90-y}Cr_yZr₁₀ alloys prove further heterogeneity of the clusters or the existence of two-cluster.

3.3 Re-entrant spin glass state and two-cluster model

Re-entrant spin glass state is one of the important magnetic behaviors for a-Fe_{100-x}Zr_x alloys. It has been explained qualitatively with cluster model.^{3),10)} Here, based on the located energy minimum and two-cluster models, the re-entrant spin glass behavior is explained phenomenologically. It proves directly the existence of bistable magnetization state and thermal activation which cause the observed hysteresis loop and time-dependent magnetization (magnetic viscosity)¹⁰⁾. It is assumed that there exist two mean spin clusters ("A" and "B") corresponding to the bimodal $P(H_{hf})$ distribution in the system, their volumes are V_1 and V_2 respectively, and their saturated magnetization values are M_{s1} and M_{s2} respectively. Comparing with the bimodal $P(H_{hf})$ distribution (peak I and peak II), the V_1 (V_2) value is proportional to the area of peak I (II), and the M_{s1} (M_{s2}) value is proportional to the mean hyperfine field of the peak I (II). Therefore, so long as the $P(H_{hf})$ distribution are obtained, we can get the α and β values, here, $\alpha = V_1 / V_2$, $\beta = M_{s1} / M_{s2}$. The mean spin clusters "A" and "B" are assumed to be the single domain particles and to have identical uniaxial anisotropy. The total normalized magnetic free energy may be expressed as¹¹⁾

$$\varepsilon = E / (KV_2) = [\alpha \sin^2 \theta_1 + \sin^2 \theta_2] + j_1 \cos(\theta_1 - \theta_2) + j_2 \cos^2(\theta_1 - \theta_2) - h[\alpha \beta \cos(\psi - \theta_1) + \cos(\psi - \theta_2)] \quad (2)$$

where θ_1 (θ_2) is the angle between the magnetization $\vec{M}_{s1}$ ($\vec{M}_{s2}$) and the easy axis. ψ means the angle between the applied magnetic field $\vec{H}$ and the easy axis. $j_1 = J_1 / (KV_2)$, $j_2 = J_2 / (KV_2)$ are normalized quantifies. J_1 and J_2 are the bilinear and biquadratic exchange constants respectively. $h = HM_{S2} / K$. The equilibrium conditions are

$$\partial \varepsilon / \partial \theta_1 = 0, \quad \partial \varepsilon / \partial \theta_2 = 0, \quad (3a)$$

$$\partial^2 \varepsilon / \partial^2 \theta_1 \geq 0, \quad \partial^2 \varepsilon / \partial \theta_1 \partial \theta_2 \geq 0$$

$$\text{and } \partial^2 \varepsilon / \partial^2 \theta_1 \bullet \partial^2 \varepsilon / \partial^2 \theta_2 - (\partial^2 \varepsilon / \partial \theta_1 \partial \theta_2)^2 \geq 0. \quad (3b)$$

For the given values of α, β, j_1, j_2 , the metastable magnetic states of the system can be determined by the initial values of θ_1, θ_2 and the equilibrium conditions. Fig.4 shows a typical hysteresis loop, which explains the experimental loops in Ref.5 and 10. In fig.4, the curve "OP" is corresponding to the single stable state, while the curve "JKO" is corresponding to the bistable states. It is assumed that the occupation probabilities and energies referring to the two distinct metastable configuration are n_i and ε_i ($i=1,2$), and the energy of the potential hill between two metastable states is ε_3 . The barrier height δ_{ij} from the metastable state i to j passing through the potential hill can be expressed as follow: $\delta_{ij} = (\varepsilon_3 - \varepsilon_i)KV_2$. For the system containing two metastable states, we can get $n_i(t)$ as follow:¹¹⁾

$$n_i(t) = n_i(\infty)[1 - \exp(-t/\tau)] + n_i(0)\exp(-t/\tau), \quad (4)$$

where $1/\tau = \nu_0\{\exp[-\delta_{12}/(K_B T)] + \exp[-\delta_{21}/(K_B T)]\}$, and $n_i(\infty) = 1/(1 + \exp[-(\delta_{12} - \delta_{21})/(K_B T)])$, τ is the relaxation time. The reduced magnetization of the system can be expressed as follow:

$$M = \sum_i n_i(t) \cos \theta_i = n_1(t) \cos \theta_1 + n_2(t) \cos \theta_2 \quad (5)$$

Fig.4 The typical hysteresis loop of the system, the parameters are selected as follow: $\alpha = \beta = 1$, $j_1 = 0.65$, $j_2 = 1.38$, $\theta_1 = -\theta_2$.

where $\cos \theta_i$ means the reduced magnetization of i th metastable state, $\sum_i n_i(t) = 1$.

According to the hysteresis loop and Eqs.(4)(5), and setting $t=1s$, $KV_2 / K_B = 10^3 K$, $h=0.2$ and $\nu_0 = 10^9$, we can get the temperature dependence of the zero-field-cooled and field-cooled magnetization as seen in Fig.5. For the zero-field-cooled themomagnetic curve, $n_1(0) = n_2(0) = 0.5$. But for the field-cooled ($h=0.2$) themomagnetic curve, $n_1(0) = n_1(\infty)$. According to Eq.(4), we can derive that $n_1(t) = n_1(\infty)$. The zero-field-cooled and field-cooled themomagnetic curves as seen in Fig.5 reveal the re-entrant spin glass behavior⁵⁾. The quantitative fitting and study is in progress.

In summary, the existence of two clusters has been proved by Mossbauer spectroscopy, magnetization and the calculated re-entrant spin glass behavior.

Fig.5 Thermomagnetic curve in two-cluster model. Dotted line shows the zero-field-cooled one. Solid line means the field-cooled one.

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