Distributed exchange interactions and temperature dependent magnetization in amorphous $Fe_{88-x}Co_xZr_7B_4Cu_1$ alloys

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The temperature dependence of the magnetization for $Fe_{88}Zr_7B_4Cu_1$ amorphous alloy has been measured. $M(T)$ has been fit using a Handrich–Kobe model with a modified Brillouin function with an additional exchange fluctuation term. Here for the first time, an asymmetrical distribution of the exchange interactions is proposed based on empirical knowledge of the Bethe–Slater curve. A two-parameter exchange fluctuation is shown to give significantly better fits to $M(T)$ for these amorphous alloys. © *1999 American Institute of Physics.* [S0021-8979(99)76608-9]

INTRODUCTION

Nanocrystalline alloys are being explored as soft magnetic materials. The development of premiere soft magnetic materials with high saturation magnetization and excellent soft magnetic properties at elevated temperatures is important for the performance of magnetic devices such as electric engine rotors and transformers. These materials can have α-FeSi,[1] α-Fe,[2] or α-FeCo[3] nanocrystals that are produced as the product of primary crystallization of an amorphous precursor. Of interest are the intrinsic magnetic properties of the amorphous precursors to these nanocrystalline materials.

Amorphous alloys have reduced Curie temperatures, due to alloying with glass forming elements,[4] as well as distributed exchange interactions which alter the temperature dependence of the magnetization $M(T)$.[5] A mean field theory for the temperature dependence of the magnetization in amorphous alloys has been proposed by Handrich and Kobe.[5] In this theory, Handrich–Kobe proposed an expression for the reduced magnetization $\sigma(T)=M(T)/M(0\ \mathrm{K})$ which consisted of a modified Brillouin function with an exchange parameter reflecting the distribution of nearest neighbor positions in the amorphous phase. This reduced magnetization is expressed as:

$$\sigma(T)=\tfrac{1}{2}\{B_s[(1+\delta)x]+B_s[(1-\delta)x]\}, \tag{1}$$

where

$$x=\frac{3S}{S+1}\frac{\sigma}{t},\quad t=\frac{T}{T_c} \tag{2}$$

are the arguments of a conventional (spin-only) Brillouin function. Further the exchange fluctuation parameter is defined as $\delta=\sqrt{\langle\Delta J^2\rangle/\langle J\rangle^2}$. This parameterizes the root mean square (rms) fluctuation in the exchange interaction. The rms exchange fluctuation has been suggested to have a T dependence of the form:[6] $\delta=\delta_0(1-t^2)$. We have found that for our alloys this proposed T dependence does not improve the quality of the fits to the experimental $M(T)$ data. Instead, we propose an extension of the theory, which considers asymmetric exchange fluctuation terms as described below.

The dependence of the nearest neighbor exchange on atomic spacing is qualitatively well described by the Bethe–Slater curve. The position of elemental Fe, Co, and Ni, for example, on the Bethe–Slater curve has been used to explain the relative magnitudes of their ferromagnetic Curie temperatures.[7] The Bethe–Slater curve is asymmetric and fluctuations in interatomic spacing (e.g., in the amorphous state) will not necessarily give rise to a symmetric distribution of exchange interaction. We suggest using an asymmetric exchange fluctuation term in the mean field theory of the temperature dependent magnetization of an amorphous alloy. We demonstrate that this gives a better description of $M(T)$ for one of the amorphous ($Fe_{88}Zr_7B_4Cu_1$) alloys studied here.

EXPERIMENTAL PROCEDURE

Alloys of composition $Fe_{88-x}Co_xZr_7B_4Cu_1$ ($x=0$, 44, and 80) were prepared by arc melting of electrolytic Fe, Co, Zr, Fe_3B, and Cu in an argon atmosphere.[3] Amorphous ribbons were produced from the ingots using a single wheel melt spinning technique. A small positive pressure of argon was then used to quench the molten alloy onto the Cu–Be wheel. The wheel speed was 35 m/s and the ribbons were approximately 1 mm in width and 20–50 μm in thickness.

The amorphous structure was determined by conventional ($\mathrm{Cu}\,K_\alpha$ radiation) and synchrotron x-ray diffraction (using x rays with a 1.74 Å wavelength). A broad amorphous scattering peak was observed as illustrated in Fig. 1, for the synchrotron scattering experiment ($x=80$ sample). The center and the full width at half maximum were determined as shown in Fig. 1 and used in the further analysis of the fluctuation in nearest neighbor distances. $M(T)$ for the $Fe_{88}Zr_7B_4Cu_1$ amorphous alloy has been measured using a Quantum Design MPMS2 SQUID magnetometer in an applied field of 1 T. Reentrant magnetization[8] has been observed upon crystallization of the amorphous precursor using a Lakeshore Cryotronics vibrating sample magnetometer (VSM). Fits to $M(T)$ using a Handrich–Kobe and modified Handrich–Kobe model were performed using codes written in MATHEMATICA@TM. The $Fe_{88}Zr_7B_4Cu_1$ amorphous alloy is considered in the rest of the discussion.

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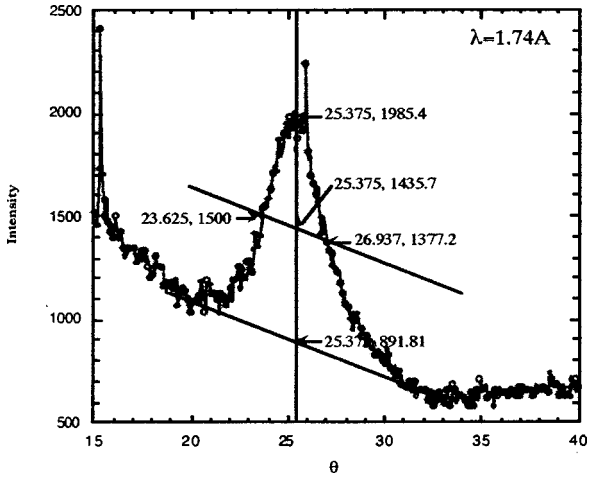

FIG. 1. Synchrotron x-ray diffraction data for an amorphous $Fe_8Co_{80}Zr_7B_4Cu_1$ alloy showing broad amorphous scattering peak, peak center, and method for determination of full width at half maximum (FWHM).

RESULTS AND DISCUSSION

The Curie temperature of the $Fe_{88}Zr_7B_4Cu_1$ amorphous alloy has been determined using a Landau theory expansion for $M(T)$ at high temperatures. The Landau theory expansion of the Helmholtz free energy (for $H=0$) per unit volume F_v is given as:

$$F_v=\tfrac{1}{2}A(T)M^2+\tfrac{1}{4}B(T)M^4,\ \frac{\partial F_v}{\partial M}=A(T)M+B(T)M^3=0. \tag{3}$$

Minimization of F leads to two solution for M: (1) $M=0$ and (2) $M^2=-A(T)/B(T)$. The simplest T dependence that we can chose within this Landau theory has a linear T dependence for the first Landau coefficient, $A=a(T_c-T)$, and no T dependence for the second Landau coefficient, i.e., B = constant. This choice leads to a T dependence of $M^2(T)=-a(T_c-T)/B$. Figure 2 shows the determination of T_c for our alloy using the Landau theory formalism. The fit given in Fig. 2 reveals a T_c of 301 K.

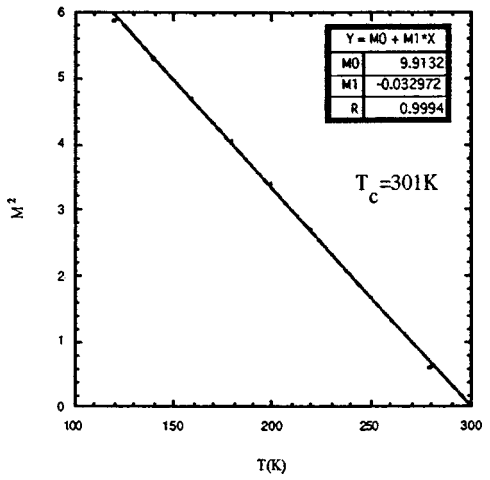

FIG. 2. Plot of M^2 vs T ($H=1$ T) for amorphous $Fe_{88}Zr_7B_4Cu_1$ alloy used to determine the Curie temperature T_c.

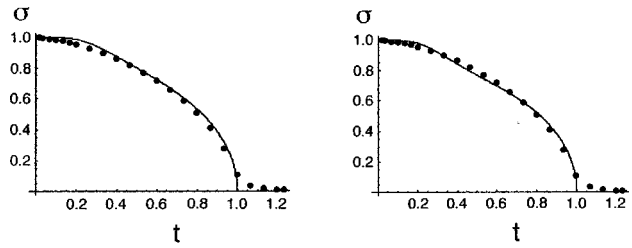

FIG. 3. (a) Reduced magnetization m as a function of reduced temperature t, an amorphous $Fe_{88}Zr_7B_4Cu_1$ alloy fit with a single δ (data points, solid line is a are fit with $\delta=0.55$,); and (b) the same data fit with asymmetric exchange fluctuation parameters $\delta_+^0=\delta_+^0=0.55$ and $\delta_+^1=0.0$ and $\delta_-^1=-0.15$.

Equation (1) was used to estimate a δ parameter for the data of $Fe_{88}Zr_7B_4Cu_1$. Using the original Handrich–Kobe formulation, a best fit was obtained for a δ parameter of about 0.55 [Fig. 3(a)], however the theoretical fit to the experimental data was not very good. This one parameter fit is not improved substantially by the consideration of a temperature dependence[6] for δ.

The original formulation by Handrich and Kobe assumes a Gaussian distribution[7] for the exchange interactions in amorphous alloys. Here we introduce an asymmetrical distribution of the exchange interactions based on empirical knowledge of the Bethe–Slater curve. A modification is made to the Handrich–Kobe equation, which allows for two δ parameters: δ_+ and δ_-. The new equation is:

$$\sigma(T)=\tfrac{1}{2}\{B_s[(1+\delta_+)x]+B_s[(1-\delta_-)x]\}, \tag{4}$$

where δ_+ and δ_- are not necessarily the same. A better fit to the experimental data was found with an asymmetric exchange distribution function with $\delta_-=0.56$ and a smaller $\delta_+=0.48$. A four-parameter exchange fluctuation fit, with temperature dependent terms to $M(T)$ is shown in Fig. 3(b) (the parameters are discussed below) again with $\delta_-(0\text{ K})=0.56$ and $\delta_+(0\text{ K})=0.41$.

Deviation in atomic nearest neighbor distances in amorphous alloys has been estimated from x-ray scattering data. The Fe–Fe average nearest neighbor distance was estimated to be: $D_{\text{Fe–Fe}}=(1.23\lambda)/(2\sin\theta)$ where θ is taken to be the angle at the center of the amorphous peak.[9] The fluctuations in the Fe–Fe average nearest neighbor distance were estimated to be: $\Delta D_+=D_{\text{Fe–Fe}}[\theta-0.5$ full width half maximum (FWHM)$]-D_{\text{Fe–Fe}}(\theta)$ and $\Delta D_-=D_{\text{Fe–Fe}}(\theta)-D_{\text{Fe–Fe}}(\theta+0.5\,\text{FWHM})$. This analysis reveals $D=2.53$ Å and $\Delta D_+=0.17$ Å and $\Delta D_-=0.13$ Å. The Bethe–Slater curve was used to estimate fluctuations in the exchange interaction (see Fig. 4). The average atomic separation, based on the amorphous scattering peak, is divided by the appropriate diameter of the Fe $3d$ orbital for estimating J_{ex}.[10] The Fluctuation in interatomic spacing allows us to estimate the resulting fluctuation in J_{ex}. A more rigorous quantitative analysis would use the scattering peak to determine the radial distribution function and then arrive at the distribution function for the exchange energies. A quantitative analysis of the low temperature magnetization in amorphous Fe-based alloys, based on spin-wave theory, has

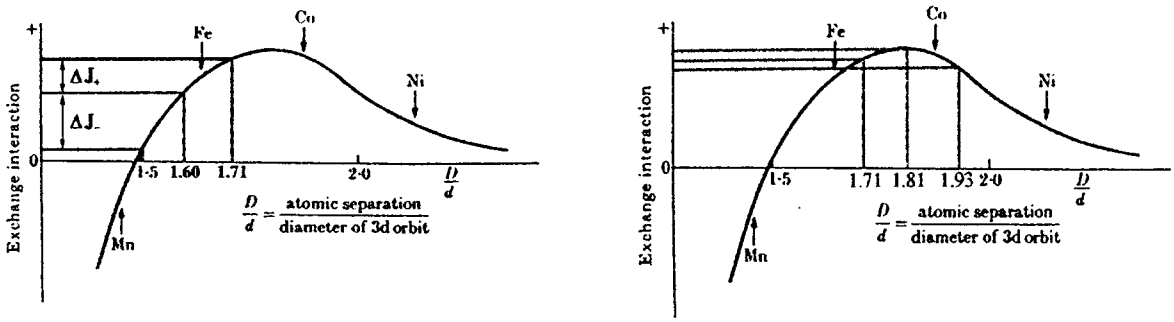

FIG. 4. Bethe–Slater curves for (a) Fe-rich and (b) Co-rich amorphous alloys, respectively, showing experimentally determined fluctuations in interatomic distances and resulting fluctuations in the exchange interactions.

been reported by Hasegawa.[11] The exchange interactions in the amorphous alloys have been determined to be quite short range.[12,13]

An explanation is suggested for the relative invariance of $M(T)$ in Co-based alloys to disorder as compared with Fe-based alloys. In the amorphous phase, structural fluctuations give rise to fluctuations in the exchange interactions. These cause a depression of the reduced magnetization versus reduced temperature curve as illustrated above. A first order theory can be offered by considering a Taylor series expansion of the exchange interaction as a function of nearest neighbor spacing of

$$J_{\mathrm{ex}} = J_{\mathrm{ex}}^0 + \left(\partial J_{\mathrm{ex}}/\partial x\right)_{x_0} \Delta x + \ldots \quad .$$

It can be seen that alloys which lie near the peak in the Bethe–Slater curve (e.g., Co, FeCo), will be relatively insensitive to fluctuations in the interatomic separation since $dJ/dx \sim 0$. On the other hand, alloys for which J_{ex}^0 lies well away from the peak (e.g., Fe- and Ni-based alloys for which $dJ/dx \neq 0$) will have J_{ex} be more sensitive to fluctuations in the interatomic separation. It should be noted that the 12 at % B, Zr, and Cu additions to our amorphous alloys will undoubtedly shift J_{ex}^0 to the left of the elemental values.

Figure 4 illustrates this formalism for the Fe- and Co-rich amorphous alloys in our series. The values for D, ΔD_+, and ΔD_- are determined from x-ray data. The exchange fluctuations, δ_+ and δ_-, are determined from the Bethe–Slater curve. The proximity of Co to the peak in the Bethe–Slater curve results in relatively small (and more symmetric) fluctuations in the exchange energy. The fact that J_{ex}^0 for Fe containing alloys lies well to the left on the Bethe–Slater curve results in larger and asymmetric fluctuations in the exchange energy. We conclude that in different alloys systems positional and chemical disorder can have a different relative importance. It is suggested that a more appropriate parameterization of the exchange fluctuation may consider both asymmetry and temperature dependence and be of the form:

$$\delta_+ = \delta_+^0 + \delta_+^1(1-t^2), \quad \delta_- = \delta_-^0 + \delta_-^1(1-t^2), \tag{5}$$

where the first term reflects chemical and positional disorder and the second thermal disorder.

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