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Ferromagnetic resonance evidence for superparamagnetism in a partially crystallized metallic glass

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Ferromagnetic resonance (FMR) measurements have been performed on samples of the metallic glass $Fe_{40}Ni_{40}P_{14}B_6$ (Metglas 2826) annealed at 350 °C for several periods of time. Two absorption lines are seen, one due to the amorphous phase and another to a crystalline phase. The apparent anisotropy field of the crystalline phase, as calculated from FMR data, increases with annealing time up to an annealing time of 100 h. The results are consistent with the assumption that particles of the crystalline phase smaller than about 300 Å exhibit superparamagnetic behavior. Calculations based on this assumption yield a value for the Avrami exponent, $n = 1.52$, which is close to the value obtained from linewidth-broadening measurements and consistent with parabolic growth at a constant or slightly decreasing nucleation rate.

I. INTRODUCTION

The thermal stability of metallic glasses is a subject of considerable interest, since the mechanical, electric, and magnetic properties of these amorphous alloys may be significantly changed by the onset of crystallization. Ferromagnetic resonance (FMR) spectroscopy seems to be a convenient method to study the crystallization of metallic glasses, because it is a fast, sensitive, and nondestructive technique. Until now, most FMR studies[1-8] have concentrated on measuring the linewidth as a function of the annealing time and temperature. In most cases, the linewidth increases with annealing time and temperature, at least for long annealing times. This is attributed to several factors, among them the nucleation of crystallites in the amorphous matrix. The presence of crystallites implies that what is observed is not a single resonance line, associated with the amorphous phase, but a compound line, i.e., the sum of the absorption due to the amorphous phase and the absorption due to the precipitates. Since the precipitates are crystalline, they can have a large magnetocrystalline anisotropy; it is thus expected that in some metallic glasses the first-derivative FMR absorption spectrum of annealed samples will exhibit the extra peak that occurs[9] in polycrystalline ferromagnetic samples when the magnetocrystalline anisotropy is larger than the single-crystal linewidth. In the present work such a peak is studied in annealed samples of a commercial metallic glass, Metglas 2826. The results are consistent with the assumption that crystallites smaller than a certain size exhibit superparamagnetic behavior; calculations based on this assumption yield estimates of the Avrami exponent for the phase transition, as well as of the anisotropy energy of the crystallites.

II. EXPERIMENTAL PROCEDURE

The alloy, of nominal composition $Fe_{40}Ni_{40}P_{14}B_6$, was supplied in the form of ribbons 2 mm wide and 50 μm thick. Heat treatments were carried out in air, on small pieces of the ribbon (2–4 mm long), in a tube furnace with a temperature accuracy of ±1 °C. The annealing temperature was chosen to be 350 °C because, according to previous results using this alloy,[4] crystallization at this temperature should be completed in a reasonable time (about 100 h). Annealing times of 6, 12, 32, 64, and 128 h were used so that one could follow the precipitation process from the beginning.

First-derivative FMR spectra were recorded at room temperature using an X-band Varian E-12 spectrometer. All measurements were taken with the static field parallel to the sample surface and along the long axis of the ribbon.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. FMR spectra

The FMR spectra of samples annealed for various periods of time at 350 °C are shown in Fig. 1. For annealing times shorter than about 10 h, the spectrum has a symmetric shape [Fig. 1(a)]. For medium annealing times, an extra peak is observed at low fields [Fig. 1(b)]. As annealing progresses, the field difference between this peak and the low-field peak of the main resonance curve

TABLE I. Simulation parameters for the FMR spectra of $Fe_{40}Ni_{40}P_{14}B_6$ samples annealed at 350 °C for several periods of time.

t (h)	H_A (mT)	ΔH (mT)	M (10^5 A m^{-1})
6	0	39	6.2
16	0/69	53/53	6.1
32	83	97	6.0
64	88	156	6.0
128	91	170	6.0

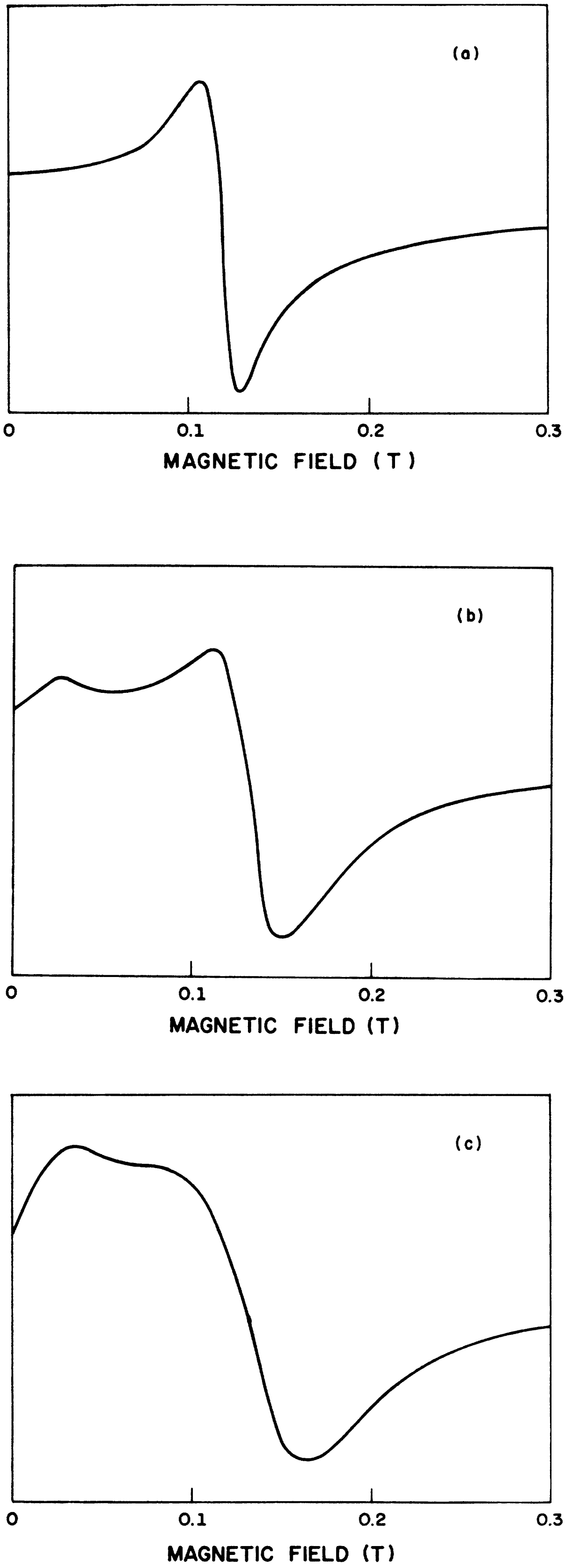

FIG. 1. Room-temperature FMR spectra of $Fe_{40}Ni_{40}P_{14}B_6$ samples annealed for various periods of time, t, at 350 °C. (a) $t=6$ h, (b) $t=16$ h, and (c) $t=32$ h.

increases [Fig. 1(c)]. Finally, for annealing times longer than 100 h, no further changes in the resonance curve are observed.

These results can be interpreted as follows: For short annealing times, the spectrum is dominated by the absorption due to the amorphous phase; for medium annealing times, one sees the sum of two spectra, one due to the amorphous phase and other to a crystalline phase; for long annealing times, the spectrum is dominated by the absorption due to the crystalline phase.

B. Simulations

Simulations based on the ideas outlined were performed with the help of a computer program developed by Taylor and Bray.[10] The resonance line was computed as the sum of two curves, one due to the amorphous phase and another to a crystal phase.

A Lorentzian shape was assumed for both curves; the curve due to the amorphous phase was taken to be isotropic, while cubic magnetocrystalline anisotropy was assumed for the curve due to the crystal phase. The simulation parameters were adjusted for the best fit to the experimental spectra. The results are shown in Table I. For an annealing time of 6 h, a reasonable fit was obtained using only the simulated curve of the amorphous phase; for 16 h, it was necessary to use both simulated curves; for annealing times of 32 h and longer, a reasonable fit was obtained using only the simulated curve of the crystal phase. In all cases, the magnetization M was calculated from the expression

$$(h\nu/g\beta)^2=H_{\mathrm{eff}}(H_{\mathrm{eff}}+M)\,, \tag{1}$$

where H_{eff} is the effective field assumed in the simulation.

C. Analysis

According to the results shown in Table I, the apparent anisotropy field of the crystal phase increases with annealing time. This behavior is typical of a system of

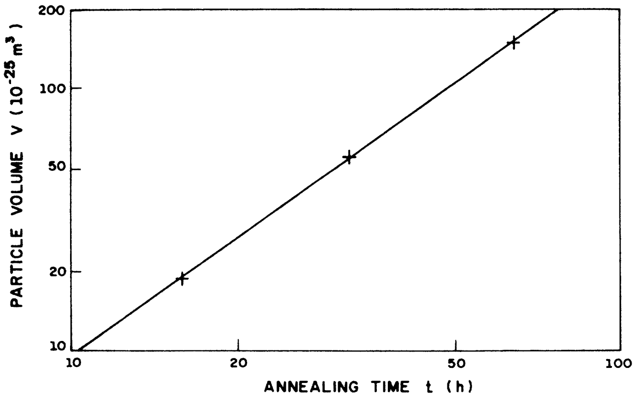

FIG. 2. Dependence of the average particle volume on the annealing time for $Fe_{40}Ni_{40}P_{14}B_6$ samples annealed at 350 °C. The straight line is a least-squares fit to the experimental points.

paramagnetic precipitates, where the apparent anisotropy is a function of particle size.[11–14] It can be shown[11] that in the case of cubic symmetry the apparent anisotropy of a collection of small particles is given by

$$H_A^{\mathrm{SP}}=H_A(1-10x^{-1}\coth x+45x^{-2}-105x^{-3}\coth x+105x^{-4})/(\coth x-x^{-1})\ , \tag{2}$$

where H_A is the bulk anisotropy field and

$$x=MVH/kT\ , \tag{3}$$

where M is the particle magnetization, V is the particle volume, and H is the magnetic field.

Since no changes are observed in the spectrum for annealing times longer than 100 h, one can assume that $H_A=91$ mT, i.e., that for an annealing time of 128 h particles are so large that the anisotropy attains its bulk value. In that case, the anisotropy constant (in J m^{-3}) of the crystal phase may be calculated from the measured values of M and H_A:

$$K=MH_A/2=2.73\times10^4\ . \tag{4}$$

For a particular annealing time, the average particle volume may be computed using Eq. (2) to calculate x from the ratio H_A^{SP}/H_A and Eq. (3) to calculate V. The results are shown in Table II. Notice that the data points for aging times of 6 and 128 h are not included, the first because the absorption due to the crystalline phase is too weak to be observed and the second because the aging time is so long that the anisotropy of the crystalline phase has already attained its bulk value. A least-squares fit to the experimental data (Fig. 2) yields a value for the Avrami exponent, $n=1.52$, which is close to the value obtained from linewidth measurements on samples annealed between 350 and 375 °C, $n=1.67$, and consistent with parabolic growth at a constant or slightly decreasing nucleation rate.[15]

TABLE II. Dependence of the normalized apparent anisotropy H_A^{SP}/H_A, the average particle volume V, and the average particle diameter $a=(6V/\pi)^{1/3}$ on annealing time for $\mathrm{Fe_{40}Ni_{40}P_{14}B_6}$ samples annealed at 350 °C.

t (h)	H_A^{SP}/H_A	V (10^{-25} m^3)	a (Å)[a]
16	0.758	19	150
32	0.912	57	200
64	0.967	155	300

[a] Assuming spherical particles.

One final word about the composition of the precipitates. X-ray and transmission electron microscopy measurements[16] on samples aged for 128 h at 350 °C yield a spectrum similar to that reported by Walter *et al.*[17] One may thus assume that the precipitates are mainly a $\mathrm{(Fe,Ni)_3(P,B)}$ compound, with traces of α-Fe.

IV. CONCLUSION

The results reported here suggest that measurement of superparamagnetic properties may provide a useful technique to study the annealing behavior of some metallic glasses.

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