

Origin of the perpendicular anisotropy in amorphous $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ ribbons

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The magnetic anisotropy in amorphous $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ (METGLAS® 2605S) has been studied by the determination of both surface and bulk properties using Mössbauer, x-ray, and density measurements. Upon annealing above 650 K, a substantial anisotropy with an easy direction perpendicular to the ribbon plane develops. It is proposed that the origin of this out-of-plane anisotropy, also observed for other amorphous ribbons, is a compressive stress from the formation of higher-density crystalline surface layers. The compressive stress produces the perpendicular anisotropy in the ribbon bulk through positive magnetostriction.

I. INTRODUCTION

Recently, a number of interesting results on the magnetic anisotropy of amorphous ferromagnetic ribbons have been reported. Particularly important is the observation of an out-of-plane anisotropy in various annealed samples¹⁻⁵ despite the large demagnetizing effect that would favor the moments to lie in the ribbon plane. Brown and co-workers² found that by annealing $\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$ foils at 600 K for 1 h, the magnetization became predominantly perpendicular to the foil surface. Similar results were also observed by Chien³ for $\text{Fe}_{80}\text{B}_{20}$ annealed at 600 K, by Chien and Hasegawa⁴ for $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ annealed at 545 K for 2 d, and by Schurer and Morrish⁵ for $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ annealed at 650–675 K for 10 h. Schurer and co-workers⁶ have also studied the perpendicular anisotropy of $\text{Fe}_{78}\text{B}_{12}\text{Si}_{10}$ as a function of temperature and found that the anisotropy developed rapidly above 600 K and reached a maximum value at 710 K. At this point, it should be emphasized that this perpendicular anisotropy exists even for free unstrained ribbons and is not caused by external stresses like clamping of the samples. In this paper, we report on the observation of the perpendicular anisotropy of another amorphous material $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$. Further, a model, based on observed differences between the surface and bulk properties, is proposed for the origin of the anisotropy.

II. EXPERIMENTAL

Amorphous $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ (METGLAS® 2605S) in the form of a ribbon 2.54 cm wide and 38 μm thick was obtained from the Allied Chemical Corporation. The samples cut from the ribbon roll were annealed in a helium atmosphere at various temperatures ranging from 400 to 1200 K for a fixed period of time, 20 min. Mössbauer spectra, with the γ ray perpendicu-

lar to the ribbon plane, were collected with a constant acceleration spectrometer that had linewidths of 0.25 mm/s for the inner lines of an iron absorber 12.7 μm thick. No clamping of the samples was used to avoid any effect of external stresses while Mössbauer spectra were taken at room temperature. In addition to the usual transmission geometry ^{57}Fe Mössbauer spectra were also accumulated by detecting 7.3 keV conversion electrons with a He- CH_4 flow proportional counter. The samples were checked by taking x-ray-diffraction patterns with a diffractometer (Mo $K\alpha$ radiation) equipped with a step-scanning mechanism. Densities were determined by comparing specimen weight in air and Bromoform (CHBr_3 , density of 2.865 g/cm³) at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 1 shows Mössbauer spectra taken at room temperature for the $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ samples annealed at various temperatures, T_A for 20 min. As T_A increases, the intensities of the second and fifth lines decrease while those of the first and sixth lines increase.

Information about the directions of the magnetic moments can be obtained from the relative intensities of Mössbauer absorption lines. For the 14.4-keV γ rays of ^{57}Fe , the relative intensity ratio of the second to the first or the fifth to the sixth lines is given by $A_{2,5}/A_{1,6} = 4(\sin^2\theta/[3(1 + \cos^2\theta)])$, where θ is the angle between the γ ray and the direction of the magnetic hyperfine field. The ratio $A_{2,5}/A_{1,6}$ can vary from 0 to $\frac{4}{3}$ as θ changes from 0 to 90°.

Mössbauer spectra taken at room temperature for the annealed $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ samples show that the area ratio $A_{2,5}/A_{1,6}$ (Fig. 2) decreases rapidly above the annealing temperature, $T_A = 650$ K, and becomes 0.32 at $T_A = 690$ K, demonstrating the development of an anisotropy with an easy direction perpendicular to the

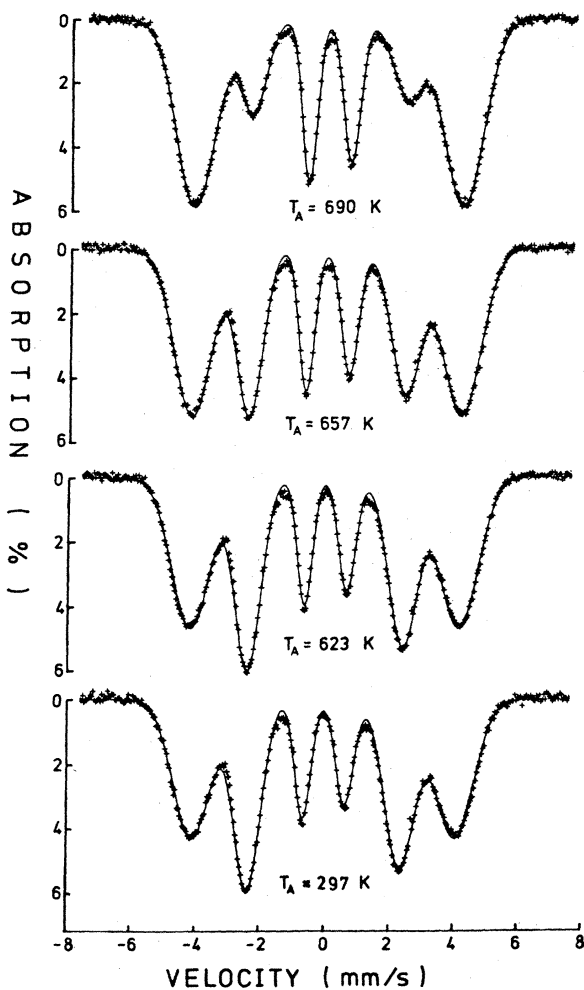


FIG. 1. Mössbauer spectra of amorphous $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ at room temperature after annealing at T_A for 30 min.

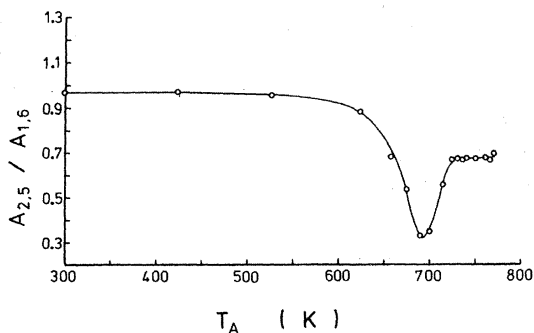


FIG. 2. Areal ratio $A_{2,5}/A_{1,6}$ of the absorption lines 2 and 5 to the outer lines 1 and 6 at room temperature as a function of the annealing temperature, T_A .

ribbon plane. In order to find out the origin of this perpendicular anisotropy, the following series of experiments were carried out with the sample annealed at 690 K.

A. Bulk crystallization

The first experiment is to determine the degree of bulk crystallization for the sample annealed at 690 K. Since the six-line patterns of the crystalline phase overlap with that of the amorphous phase at room temperature, Mössbauer spectra were taken at 470 K for two samples annealed at 690 and 727 K, respectively, for 20 min. Another advantage of taking Mössbauer spectra at 470 K is that raising the temperature tends to enhance the crystalline peaks relative to the amorphous ones because the recoil-free fraction, f_R , of the crystalline phase⁷ is higher than that of the amorphous phase by a factor of 1.39 at room temperature. The reason is a higher f_R factor (corresponding to higher Debye temperature Θ) decreases much more slowly with increasing temperature than a lower f_R factor according to the well-known expression

$$f_R = \exp \left[-\frac{3E_R}{2k\Theta} \left(1 + 4 \frac{T^2}{\Theta^2} \int_0^{\Theta/T} \frac{x dx}{e^x - 1} \right) \right],$$

where E_R is the recoil energy. Indeed, comparison of Fig. 3(b) with the Mössbauer spectrum of the sample taken at room temperature shows that the area ratio of the crystalline to amorphous peaks is enhanced by a factor of 2.30 as the temperature is increased from room temperature to 470 K. Thus, the overall areal enhancement factor of the crystalline phase relative to the amorphous phase in the Mössbauer spectrum taken at 470 K is $(1.39)(2.30) = 3.20$. It is estimated from the Mössbauer spectrum taken at 470 K for the

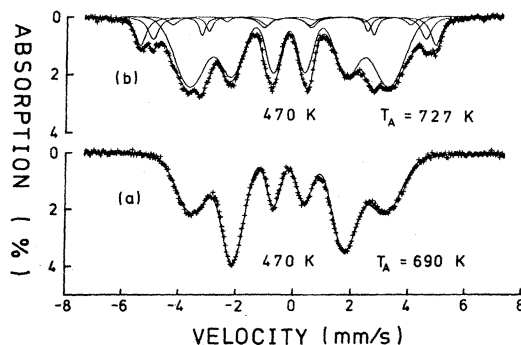


FIG. 3. Mössbauer spectra of $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ at 470 K after annealing at 727 and 690 K for 20 min. For these spectra only, the samples were clamped between two Be foils in order to get good thermal contact.

sample⁷ annealed at $T_A = 714$ K that a crystalline phase with abundance larger than 0.2% should be detectable by this method. The crystalline phase has been identified as an Fe-9 at. % Si alloy.⁷ By comparing Fig. 3(a) with Fig. 3(b) it is clear that no crystalline peaks are seen for the sample annealed at 690 K. This implies that the combined abundance of the crystalline phase including both bulk and surface crystallization is less than 0.2%.

B. X-ray diffraction

In the second experiment, x-ray-diffraction patterns were obtained for the sample annealed at 690 K. The surfaces of the sample have different appearances; one side is shiny and the other dull. X-ray-diffraction patterns taken from both surfaces are also different as shown in Fig. 4; a small crystalline peak was observed on the top of the broad amorphous peak near the Bragg angle $2\theta = 20^\circ$ for the dull side whereas no such peak was seen for the shiny side. Since only a layer about $3 \mu\text{m}$ at the surface contributes to the diffracted intensity for $\theta = 10^\circ$, these above two results suggest that one of the surface-layers is partially crystallized whereas the bulk part is still in the amorphous state.

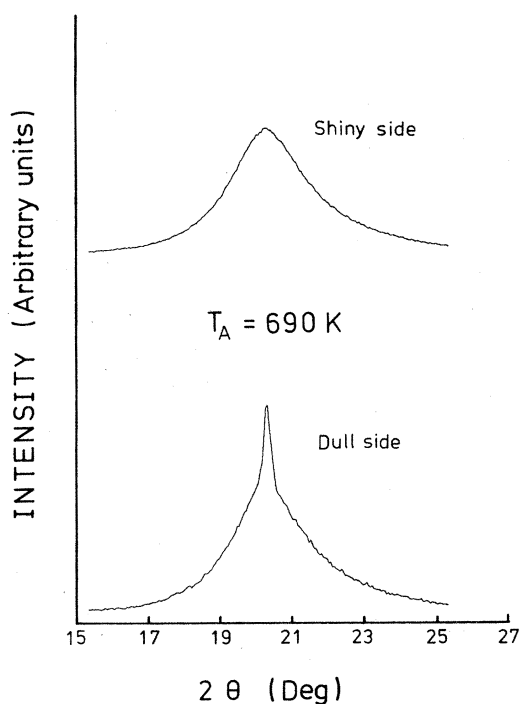


FIG. 4. X-ray diffractograms of both surfaces of $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ foil at room temperature after annealing at 690 K for 20 min.

C. Conversion-electron Mössbauer spectra

In order to confirm the surface crystallization, 7.3-keV conversion-electron Mössbauer spectra were taken for the both surfaces of the sample annealed at 690 K. The depth of sample surface examined is only on the order of 2000 Å because the 7.3-keV electrons have relatively low penetrating power.⁸ Figure 5(a) shows that the area ratio of the crystalline to the amorphous lines is 0.59. Taking into account the result⁷ that the completely crystallized sample has a larger recoil-free fraction than the amorphous sample

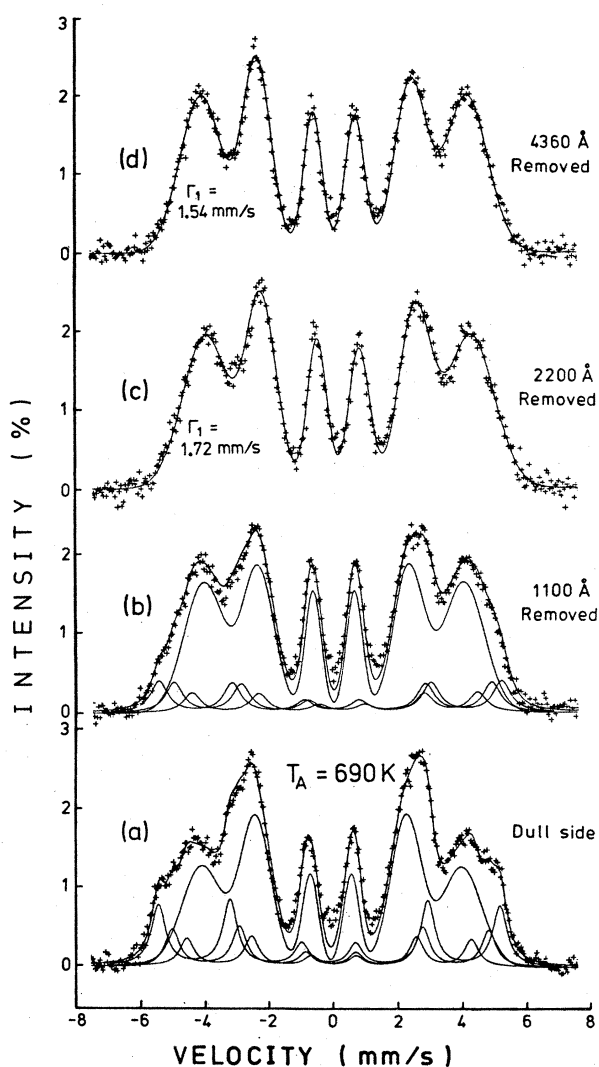


FIG. 5. 7.3-keV conversion-electron Mössbauer spectra taken from the dull-side surfaces of $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ foils at room temperature after annealing at 690 K for 20 min; (a) as prepared, (b), (c), and (d) after surface layers of thicknesses 1100, 2200, and 4360 Å were removed. Γ_1 represents the average linewidth of the two outer lines.

by a factor of 1.39, the above area ratio implies that about 30% of the surface layer on the dull side is crystallized. On the other hand, the shiny side shows only line broadening, as illustrated in Fig. 6. The average linewidth of the two outermost lines, Γ_1 is given in Figs. 5 and 6.

In order to estimate the thicknesses of the crystallized surface layers, 7.3-keV conversion-electron Mössbauer spectra were taken for each surface after removing successive surface layers. The surface layers have been removed by polishing softly by a finger tip with polishing powder soaked with alcohol, and the thickness of a surface layer removed has been determined by measuring the weight of the sample before and after polishing. The results in Figs. 5 and 6 show that the surface layers of thickness about 4000 and 100 Å are crystallized on the dull and shiny side, respectively.

Another important result from Figs. 5(a) and 6(a) concerns the relative intensities of Mössbauer six-line patterns; the intensities of the second and fifth lines are greater than those of the first and sixth lines, namely, $A_{2,5}/A_{1,6} = 1.10$ and 1.13 for the dull and shiny side, respectively. These ratios are in marked contrast with the 0.32 value for the transmission Mössbauer spectrum for the same sample, shown in Figs. 1 and 2. In other words, the magnetic moments in the surface layers are close to parallel to the ribbon

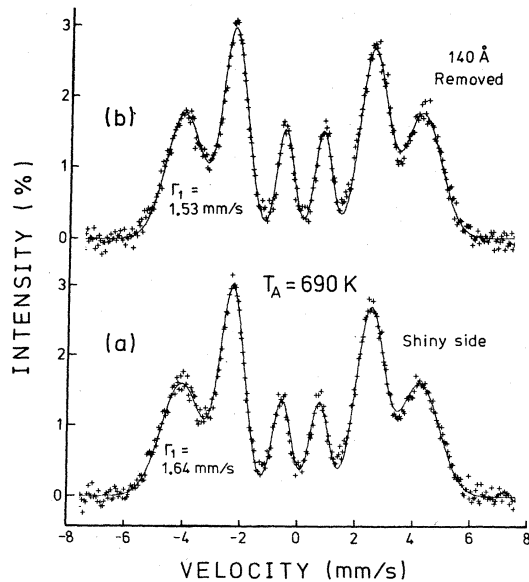


FIG. 6. 7.3-keV conversion-electron Mössbauer spectra taken from the shiny-side surfaces of $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ foils at room temperature after annealing at 690 K for 20 min; (a) as prepared, and (b) after a surface-layer of thickness 140 Å was removed. Γ_1 represents the average linewidth of the two outer lines.

plane, whereas those in the bulk part of the sample are mostly perpendicular to the plane. It should be emphasized at this point that the tendency of the $A_{2,5}/A_{1,6}$ ratio to increase with increasing removal of the surface layer is not a result of stresses induced by the mechanical polishing because electrolytical thinning of the sample in an electrolyte consisting of 90 parts ethyl alcohol and 10 parts perchloric acid yielded similar results.

D. Density

Density measurements show that a completely crystallized sample has a density of $7.49 \pm 0.01 \text{ g/cm}^3$, much larger than the $7.28 \pm 0.01 \text{ g/cm}^3$ for the as-quenched sample, or the $7.29 \pm 0.01 \text{ g/cm}^3$ for the sample annealed at 690 K. The implication is that the partially crystallized surface layers contract, thereby exerting compressive stress on the bulk amorphous portion of the sample. This compressive stress could influence the directions of the magnetic moments in the amorphous portion through magnetostriction.

E. Magnetostriction

In order to determine the existence and sign of magnetostriction in the sample annealed at 690 K, tensile stresses were applied parallel to the foil plane of the sample while Mössbauer spectra were collected. The results in Fig. 7 show that the areal ratio $A_{2,5}/A_{1,6}$ increases from 0.32 as the tensile stress is increased, and reaches a saturation value of 1.24 at

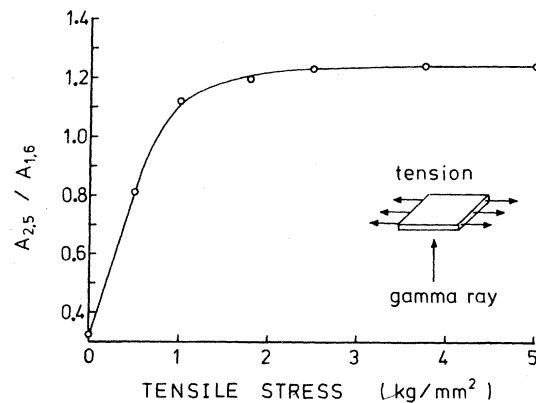


FIG. 7. Room-temperature areal ratio $A_{2,5}/A_{1,6}$ of the 2,5 and 1,6 Mössbauer absorption lines as a function of tensile stress applied parallel to the ribbon plane of the $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ sample annealed at 690 K for 20 min.

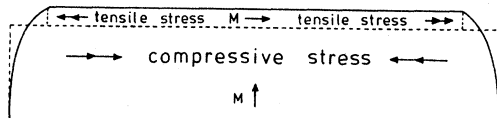


FIG. 8. Schematic representation of the proposed model; only one side of the ribbon is shown.

the tensile stress of 2.5 kg/mm^2 . Similar experiments⁹ with an as-quenched $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ sample resulted in a saturation value of 1.25 at the tensile stress of 9 kg/mm^2 , thus a significant enhancement of the magnetostriction occurs after annealing at 690 K. In summary, the sample annealed at 690 K is highly magnetostrictive and the sign of the magnetostriction is positive.

F. Proposed model

Based on the above experimental observations, we propose the following model. The origin of the perpendicular anisotropy is the compressive stress from the formation of higher-density crystalline surface layers. As illustrated in Fig. 8, the compressive stress in the bulk amorphous region forces the magnetic moments to align perpendicular to the ribbon plane through positive magnetostriction. On the other hand, the partially crystallized surface-layers are under tensile stress which forces the magnetization inside the layers to be parallel to the ribbon plane, thus leading to the in-plane anisotropy observed in the conversion-electron Mössbauer spectra.

Finally, in order to confirm this model, Mössbauer spectra were taken for the two samples whose dull or shiny surface layers were removed. This procedure should eliminate the origin of the compressive stress. Indeed, Mössbauer spectra of these samples show that the perpendicular anisotropy disappears, as demonstrated in Fig. 9. Furthermore, elimination of either surface layer resulted in curling in such a way that the surface on the eliminated side became convex, demonstrating the relief of tension on that surface.

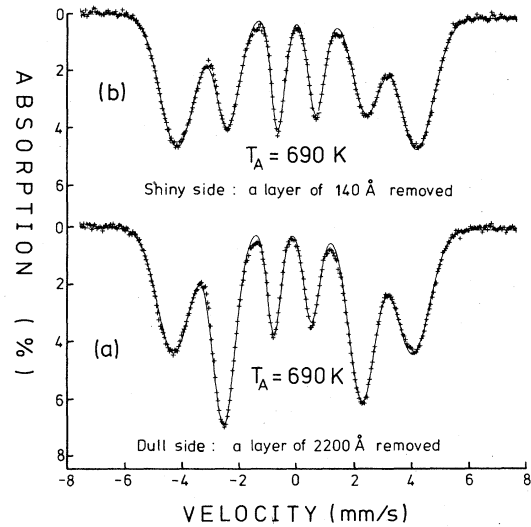


FIG. 9. Mössbauer spectra of $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ at room temperature after annealing at 690 K for 20 min; (a) after a surface layer of thickness 2200 \AA was removed on the dull side and (b) after a surface layer of thickness 140 \AA was removed on the shiny side.

Figure 2 shows that the areal ratio $A_{2,5}/A_{1,6}$ increases rapidly above $T_A = 700 \text{ K}$ and finally reaches a value of 0.67 which corresponds to the random orientation of magnetic moments. Actually, bulk crystallization⁷ of $\text{Fe}_{82}\text{B}_{12}\text{Si}_6$ starts above $T_A = 700 \text{ K}$ and is completed at $T_A = 773 \text{ K}$ when the annealing time is fixed to be 20 min. Therefore, the rapid disappearance of the perpendicular anisotropy above $T_A = 700 \text{ K}$ is the result of bulk crystallization inside the sample and subsequent weakening of the compressive stress by the decrease of density difference between the surface layers and the bulk part.

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