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Intrinsic magnetic properties of ultrathin amorphous $Fe_{70}B_{30}$/Ag multilayers

H. Tang,* R. J. Hicken,† and J. C. Walker
The Henry A. Rowland Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

Gang Xiao
Department of Physics, Brown University, Providence, Rhode Island 02912

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We report the observation of perpendicular magnetization in ultrathin amorphous $Fe_{70}B_{30}$/Ag multilayer films by means of Mössbauer spectroscopy. In contrast to other techniques that require the application of an external magnetic field, the *field-free* condition of Mössbauer spectroscopy allowed the intrinsic magnetic properties of ultrathin films to be studied. Our study indicates that at elevated temperatures an external field may easily alter the spontaneous magnetization in an ultrathin film with very small effective anisotropy and thus obscure its intrinsic magnetic properties. By virtue of the microscopic probing capability of Mössbauer spectroscopy, the surface magnetic properties of thin amorphous $Fe_{70}B_{30}$ films have also been studied.

In recent years magnetism in ultrathin films with thicknesses ranging from a few Å to a few tens of Å has been the subject of extensive studies.[1] One of the most important quantities characterizing a ferromagnetic thin film is the uniaxial magnetic surface anisotropy, which is induced due to the breaking of translational symmetry at a surface. In Néel's language,[2] the magnetic surface anisotropy is described by an energy term $E_S = -K_S \cos^2\theta$, where θ is the angle between the magnetization and the film normal while K_S is the magnetic surface anisotropy constant. The surface anisotropy may favor either a perpendicular ($K_S > 0$) or an in-plane ($K_S < 0$) magnetization. On the other hand, the dipolar interaction energy (also commonly known as shape anisotropy) always favors an in-plane magnetization in a thin film. Therefore, for an amorphous film in which bulk magnetocrystalline anisotropies can in general be ignored, the magnetization orientation is solely determined by the competition between the surface and shape anisotropy. Since the surface anisotropy energy is proportional to the area of a film whereas the dipolar interaction energy is proportional to its volume, surface anisotropy induced perpendicular magnetization is possible *only* in ultrathin films, in which the two surfaces may assume the dominant role. Experimentally, the common wisdom is that it is trivial to determine if a thin film possesses a perpendicular or an in-plane magnetization. While this is true in most cases, we show in this paper that exceptions do exist under certain conditions, and then the determination of the easy magnetization direction for a thin film becomes nontrivial.

The magnetic system we chose to study was that of amorphous $Fe_{70}B_{30}$/Ag multilayers whose surface anisotropy has been investigated in great detail.[3–5] The amorphous nature eliminates the complication of bulk magnetocrystalline anisotropies so that only the surface and shape anisotropies need to be considered. A peculiarity associated with these thin amorphous $Fe_{70}B_{30}$ films was that none showed remanent magnetization,[6] thereby preventing a direct determination of the stable magnetization configuration, i.e., perpendicular or in plane, in the field-free state. Earlier ferromagnetic resonance (FMR) studies[3–5] indicated that amorphous $Fe_{70}B_{30}$ films possess a significant perpendicular surface anisotropy whose strength, however, becomes thickness dependent for films less than 16 Å thick and monotonically approaches zero as the thickness decreases. Thus, the perpendicular resonance field was found to always remain larger than the in-plane resonance field for all film thicknesses and the conditions for perpendicular magnetization were therefore never observed. Similar results were also obtained by magnetometry in which the saturation magnetic field was measured for both parallel and perpendicular configurations.[4–6] By contrast, our Mössbauer spectroscopy (MS) measurements on the same series of samples used in the earlier FMR and magnetometry studies revealed perpendicular magnetizations for several samples consisting of ultrathin $Fe_{70}B_{30}$ layers. By a detailed analysis of the surface and shape anisotropies, we show that the contradictory experimental results can be resolved and that our MS results obtained under field-free conditions reflect the intrinsic magnetic properties of these ultrathin $Fe_{70}B_{30}$ films. In addition, by virtue of the microscopic nature of MS, we find the magnetization at the surface of the $Fe_{70}Be_{30}$ films to be significantly smaller than that in the interior of the film at room temperature.

The $(Fe_{70}B_{30})_x/Ag_{3x}$ films were prepared using a high vacuum sputtering system with two dc magnetron guns and a rotating platform.[7,8] Ag was chosen to be the spacer layer material because of its immiscibility with Fe and the minimal band overlap between Fe and Ag. Structural characterizations with x-ray diffraction and transmission electron microscopy revealed excellent layer structure.[7] Mössbauer measurements were performed at 300 K in a transmission geometry with the incident γ-ray direction parallel to the sample normal. Due to the small amount of ^{57}Fe Mössbauer isotopes contained in these multilayer samples, long acquisition times were necessary, typically over a period of 4–5 days. Each multilayer film will be denoted by its $Fe_{70}B_{30}$ layer thickness x. We note that there is a small spread, about ±10% around

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the nominal value x, in the layer thickness in each film due to the relatively large sample area and the small target-to-substrate distance. This, however, does not affect the analysis presented below.

Some Mössbauer spectra covering the $Fe_{70}B_{30}$ thickness range of interest are shown in Fig. 1. The experimental configuration is such that the relative intensity ratios of the six absorption lines in a magnetic sextet spectrum are 3:4:1:1:4:3 for in-plane magnetization, or 3:0:1:1:0:3 for out-of-plane magnetization. All of the spectra were fitted to a single sextet as well as to a magnetic hyperfine-field distribution, with the effective hyperfine field value obtained from single-sextet fit shown alongside each spectrum. From the figure it can be clearly seen that the line intensities of the second and fifth peaks in the spectra for the 5.5-, 6.6-, and 11-Å films are all diminished, establishing that the magnetizations in these films are oriented perpendicular to the film plane. The observation of perpendicular magnetization in these films, however, is completely unexpected based on earlier FMR and magnetometry measurements[4–6] that suggested that *all* samples should be magnetized in the film plane in the absence of an applied magnetic field. On the other hand, both the 13- and 17-Å films show in-plane magnetizations, as indicated by their 3:4:1:1:4:3 relative line intensity ratios. We also note that the effective hyperfine field varies significantly over the investigated $Fe_{70}B_{30}$ thickness range, indicative of a strong thickness dependence of the Curie temperature.

In order to resolve the contradiction in the easy magnetization direction determined from the present MS and earlier FMR and magnetometry measurements, we must closely examine, *under the respective experimental conditions* of FMR, magnetometry, and MS, the two competing factors that control the magnetization direction, i.e., the magnetic surface anisotropy energy (per unit volume) $u_S=-(2K_S/x)\cos^2\theta$ and the dipole interaction energy

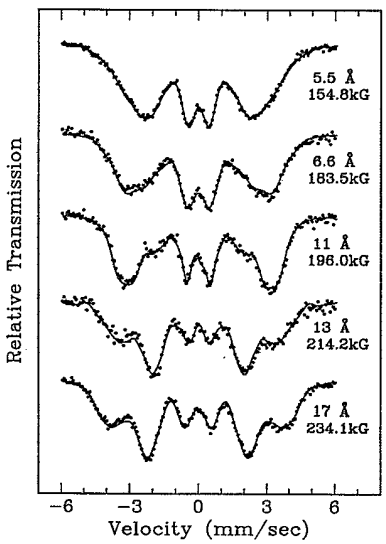

FIG. 1. Mössbauer spectra for the $(Fe_{70}B_{30})_x/Ag_{3x}$ multilayer samples measured at 300 K. Both x and the effective hyperfine field obtained from single-sextet fit are shown. Solid curves represent hyperfine-field distribution fits.

$u_D=2\pi M(T)^2\cos^2\theta$,[9] where $M(T)$ is the magnetization at temperature T. If $u_S+u_D<0$ ($u_S+u_D>0$), the magnetization direction should be perpendicular (parallel) to the plane. We first note that all of the measurements were conducted at 300 K, which is a relatively high temperature considering that bulk $Fe_{70}B_{30}$ has a Curie temperature of about 750 K and that the T_C's for some of the ultrathin films are expected to be substantially reduced from the bulk value. The fact that the surface anisotropy energy and the shape anisotropy energy are opposite in sign but nearly equal in magnitude in these ultrathin films affords a condition for relatively soft spin-wave modes,[10,11] and so the spontaneous magnetization is greatly reduced from its ground-state value due to extensive thermal spin-wave excitations. In fact, the much reduced effective hyperfine fields in the thinner films, as shown in Fig. 1, are direct evidence for the existence of soft spin-wave modes. In such films, the application of an external field of several thousand Gauss can effectively remove the anisotropy cancellation and thus eliminate the soft spin-wave modes, leading to an increase of the magnetization. Therefore, the measured magnetization under an external field may significantly exceed the spontaneous magnetization under field-free conditions. The key difference between the FMR or magnetometry measurements and the present MS measurements is that in the former an external field of a few thousand Gauss was applied owing to the nature of these techniques, whereas the latter were conducted under field-free conditions. The increased magnetization due to an external field may enhance the dipolar interaction energy such that $u_S+u_D>0$ and hence the easy magnetization direction appears to be in the film plane, as suggested by the FMR and magnetometry measurements. On the other hand, the smaller spontaneous magnetization under the field-free condition as realized in the MS experiments may satisfy $u_S+u_D<0$ so that the perpendicular magnetization configuration is stabilized.

The effect of an external field on the magnetization of an ultrathin film can be readily verified with a comparative MS study with and without an applied field. We stress here that MS is ideally suited for such a verification because of its microscopic nature which renders it completely insensitive to such complications as domain formation which would make other techniques, e.g., magnetometry, unreliable. In Fig. 2 we show the Mössbauer spectra obtained at 300 K for the 6.6-Å sample with an external field of varying strengths applied in the sample plane. In addition to the expected enhancement of the second- and fifth-line intensities (as the magnetization is forced to align with the applied in-plane field), the external field also leads to a significant enhancement of the effective hyperfine field. Since the hyperfine field is proportional to the magnetization, it follows immediately that the magnetization is also enhanced. For an external field of 2.4 kG, the enhancement is 12.4%, which translates into a 26% increase in the dipolar interaction energy over the zero-field case. As will be shown below, such an increase is more than sufficient to change the stable magnetization configuration from being perpendicular to in plane. The large effect of a relatively weak field

on the spontaneous magnetization exemplifies the magnetic instability that an ultrathin film may be subject to when its effective anisotropy becomes small.

The observed external-field-induced enhancement of the Mössbauer hyperfine field in the 6.6-Å film may also signal the existence of superparamagnetic fluctuations. Such a scenario is particularly inviting as island formation in an ultrathin film is always a possibility. However, previous transmission-electron-microscopy measurements[7] on a 10-Å film revealed continuous layer structure without any evidence of island formation. Moreover, island formation in an ultrathin film generally results in a distribution of island sizes, thereby manifesting itself in a central superparamagnetic peak in the Mössbauer spectrum due to the smaller islands whose blocking temperatures are below the measuring temperature, e.g., room temperature. Such a central feature is clearly absent in all of our spectra. In addition, the $M(H)$ characteristics for even a film as thin as 4.1 Å at room temperature is unmistakeably ferromagnetic.[7] If there exists any superparamagnetic effect in the 6.6-Å film, its blocking temperature should be significantly above 300 K for magnetometry and at least a factor of 3 higher for MS,[12] which would far exceed the Curie temperature of the film. Thus, any reduction in the magnetization, or hyperfine field, due to superparamagnetic fluctuations should be small. Most importantly, superparamagnetic fluctuations in this case would equally reduce the shape anisotropy energy and the surface anisotropy energy by exactly the same proportion and, therefore, would *not* alter the relative strengths of the two competing anisotropies. In other words, the contradictory results regarding the easy magnetization direction in these ultrathin films between the MS and earlier FMR and magnetometry measurements cannot be resolved within the framework of superparamagnetic fluctuations. As will be shown later, however, our model based on soft spin-wave modes would satisfactorily settle the discrepancies.

The spontaneous magnetizations at 300 K under the field-free condition for all samples can be derived from their corresponding effective hyperfine fields based on the following equation:

$$\frac{H_{\text{eff}}(T)}{H_{\text{eff}}(0)} = \frac{M(T)}{M(0)} \quad (1)$$

whose validity for the $Fe_{1-x}B_x$ system was shown in Ref. 13. The magnetization thus determined will be denoted by $M_0(T)$, which is to be differentiated from the field-saturated magnetization determined from magnetometry measurements[7] hitherto denoted by $M(T)$. Both $M(0)$ and $M(300\text{ K})$ for all $Fe_{70}B_{30}$ layer thicknesses have been determined in Ref. 7. As a good approximation, we may assume that the 17-Å sample is sufficiently thick to be bulklike such that its magnetization at 300 K is not affected appreciably by an external field, i.e., $M_0(300\text{ K}) \approx M(300\text{ K})$. It follows immediately from Eq. (1) that $H_{\text{eff}}(0)=270$ kG for the 17-Å sample. Since the ground-state magnetizations $M(0)$ for all samples are the same, as shown in Ref. 7, we may regard that all of the samples share the same value for the ground-state hyperfine field, i.e., $H_{\text{eff}}(0)=270$ kG as determined from the 17-Å sample. Then, the spontaneous magnetization $M_0(300\text{ K})$ for the remaining samples are readily obtained from the corresponding $H_{\text{eff}}(300\text{ K})$ values determined in the zero-field MS measurements. The magnetic surface anisotropy constant K_S for all sample thickness can be found in Ref. 4. Neglecting the angular factor $\cos^2\theta$, the relevant energies that determine the easy magnetization direction under the field-free condition, $u_S=2K_S/x$ and $u_{D0}=2\pi M_0(300\text{ K})^2$ are plotted in Fig. 3 for all $Fe_{70}B_{30}$ layer thicknesses. For comparison, the dipolar interaction energies $u_D=2\pi M(300\text{ K})^2$ evaluated with the magnetizations measured with an external field are also shown in the same figure. The results clearly show that the condition for perpendicular magnetization, $u_S+u_{D0}<0$, is satisfied for $x<12$ Å, in complete accord with the Mössbauer results. On the other hand, if the magnetization is enhanced by an external saturating field, such as in FMR or magnetometry measurements, the field-free easy direction would instead appear to be in the film plane for *all* samples.

We now discuss the surface (or interface) effects on the magnetizations of $Fe_{70}B_{30}$ films. Figure 4 shows the

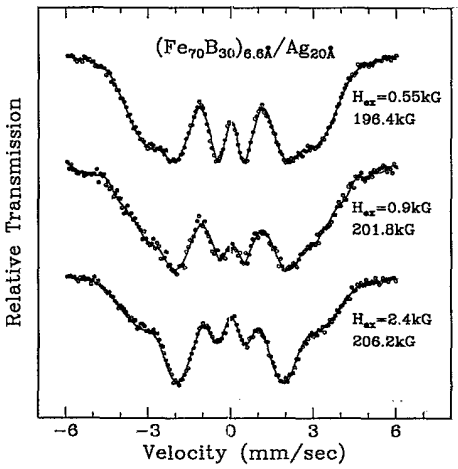

FIG. 2. Mössbauer spectra and hyperfine-field distribution fits for the $x=6.6$-Å sample measured at 300 K with several different applied fields, H_{ex}. The effective hyperfine fields obtained from single-sextet fits are also shown, in which the contribution from the applied fields has already been removed.

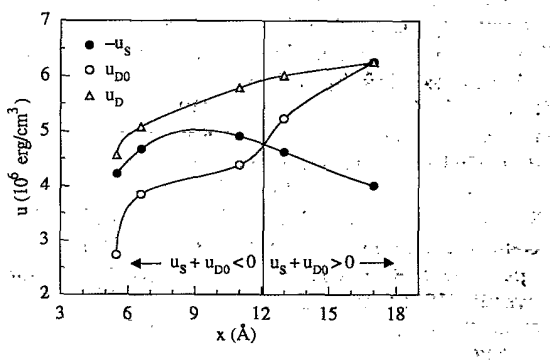

FIG. 3. Comparison of u_S, u_{D0}, and u_D for various $Fe_{70}B_{30}$ layer thicknesses, x. The solid lines through the data points are guides to the eye.

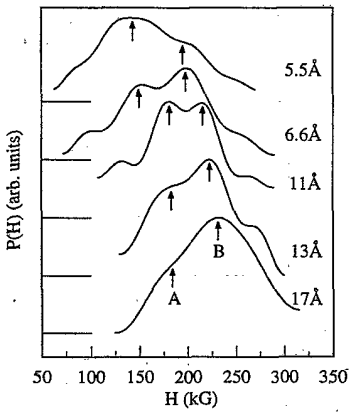

FIG. 4. Hyperfine-field distribution curves for the $(Fe_{70}B_{30})_x/Ag_{3x}$ samples at 300 K. The $P(H)$ curves have a scale of 0 to 1 and are vertically displaced against each other for clarity, and the zero reference lines are shown on the left.

hyperfine-field distributions for all of the Mössbauer spectra in Fig. 1. For clarity, only portions of the $P(H)$ curves in their respective regions of interest are shown. As indicated by the arrows in the figure, there are two prominent structures in each $P(H)$ curve. This should be contrasted with the structureless, Gaussian-like hyperfine-field distributions found in bulk amorphous $Fe_{70}B_{30}$ materials.[13–15] Clearly, the two structures are associated with the two distinct Fe sites in each amorphous $Fe_{70}B_{30}$ layer, namely the interface site and the interior site. Here we still use the term "site," which, strictly speaking, is appropriate only for crystalline materials. As the $Fe_{70}Be_{30}$ layer thickness is increased, the spectral intensity of structure B (of larger hyperfine field) increases at the expense of that of structure A (of smaller hyperfine field). Such a systematic variation suggests that structure A is associated with the interface Fe site and structure B is associated with the interior Fe site.

The above site assignment is further supported by the observation that the hyperfine field of structure A is smaller than that of structure B. This is based on the general argument that, due to the reduced coordination of magnetic nearest neighbors and possibly reduced exchange interaction at the surface, thermal spin-wave excitations are stronger at the interface than in the interior.[16–18] The results in Fig. 4 for all five samples consistently yield a value of about 50 kG for the difference between the magnetic hyperfine fields associated with the interior and interface Fe sites. We find this large difference particularly striking because ultrathin single crystalline Fe(110)/Ag(111) films at 300 K showed a difference of no more than a few kiloGauss between the hyperfine fields at the interior and at the surface.[19] It indicates that amorphous ferromagnets, at least in the case of $Fe_{70}Be_{30}$, are less coherent in the sense that nearby moments can behave very differently. This property may be related to the lack of long-range structural order in amorphous materials. From the relative intensity of structure A, we can estimate that the thickness of the interface region, where the magnetic properties are altered from those of the interior, is about 2 Å, which corresponds to about one monolayer of close-packed Fe atoms. In addition to the reduced Curie temperatures in these ultrathin films, the large reduction of the magnetization at the surface is also responsible for the reduced overall film magnetization and, therefore, the stabilization of the perpendicular magnetization configuration.

In conclusion, we have shown that the easy magnetization direction for ultrathin amorphous $Fe_{70}B_{30}$/Ag films is out of plane at room temperature. The decrease of the perpendicular surface anisotropy with the $Fe_{70}B_{30}$ layer thickness is offset by the reduction of the spontaneous magnetization due to both thin film and surface effects, thereby leading to the stabilization of the perpendicular magnetization configuration. Our study demonstrates that the easy magnetization direction in an ultrathin film may only be determined under field-free conditions, especially in the presence of soft spin-wave modes.

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*Present address: Stanford Linear Acclerator Center, P.O. Box 4349, Stanford, CA 94309.

†Present address: Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, United Kingdom.

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