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Deposition-temperature dependence of structural anisotropy in amorphous Tb-Fe films

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The anisotropic local structure in a series of amorphous $Tb_{26}Fe_{74}$ films deposited at different deposition temperatures and having different magnetic anisotropy energies have been investigated using polarization-dependent extended x-ray-absorption fine-structure measurements. Samples deposited at temperatures ≥ 300 K exhibit anisotropic pair correlations where like atomic pairs are favored in plane and unlike pairs are favored out of plane. Both the anisotropic pair correlations and the perpendicular magnetic anisotropy increase with increasing deposition temperature. In contrast, a sample deposited at 77 K was found to have isotropic pair correlations, low perpendicular magnetic anisotropy, and a large ($\approx 1\%$) in-plane compression.

In 1973 perpendicular magnetic anisotropy was discovered in amorphous rare-earth–transition-metal (*a-RM*) films.[1] In the years since, this property has been pivotal in the development of magnetic bubble and magneto-optic storage technologies. Although the literature is replete with studies of the properties of these materials, the origins of this phenomenon has remained unclear, largely because of the difficulty in measuring the local chemistry and structure of thin amorphous films. Several groups have employed short-range structural probes in attempts to find evidence for a deviation from an isotropic structure which would explain the magnetic anisotropy measured in these alloys. Cargill and Mizoguchi applied small-angle x-ray scattering,[2] D'Antonio *et al.* used total neutron scattering,[3] and Robinson, Samant, and Marinero used extended x-ray-absorption fine-structure (EXAFS) measurements;[4] but not until Yan *et al.*,[5] using a synchrotron x-ray scattering, and Harris *et al.*,[6] using polarization-dependent EXAFS, was a structural anisotropy detected in these materials.

In an earlier paper,[6] we demonstrated the existence of a structural anisotropy in *a*-TbFe films using polarization-dependent EXAFS. We also showed that heat treatment could simultaneously eliminate the structural anisotropy and reduce the magnetic anisotropy energy to a level consistent with magnetoelastic interactions between the film and substrate. EXAFS results presented in Ref. 6 suggest that the large part of the perpendicular magnetic anisotropy in *a*-TbFe is associated with anisotropic pair correlations where a greater number of like atom pairs bond in the film plane and a greater number of unlike pairs bond perpendicular to the film plane. Although similar anisotropy models have been proposed to account for magnetic anisotropy in *a-RM* systems,[1,7–9] little experimental evidence has been presented to support their existence.

Recent first-principles band-structure calculations by Coehoorn[10] suggest that the anisotropic arrangement of atoms proposed in Ref. 6 provides a magnetic anisotropy having the correct sign (perpendicular to the film plane) through a coupling of the aspherical charge cloud at the rare-earth site to the anisotropic electrostatic fields generated by the anisotropic pair correlations.

In an investigation of the processing dependence of the magnetic anisotropy in *a*-TbFe films, Hellman and Gyorgy[11] showed that the magnetic anisotropy energy in samples having the same composition increases over an order of magnitude when the deposition temperature is increased from 77 to 525 K. An enhanced perpendicular magnetic anisotropy in *a*-TbFe films deposited at elevated temperatures was also reported by Kobayashi *et al.*[12] and Takeno, Suwabe, and Goto.[13]

In this paper, we present the results of polarization-dependent EXAFS measurements performed on *a*-TbFe films that have the same compositions, $Tb_{26}Fe_{74}$, but different magnetic anisotropy energies due to different substrate temperatures used in deposition. The magnetic properties of these samples were reported earlier by Hellman and Gyorgy.[11] We find that both the anisotropic pair correlations and the perpendicular magnetic anisotropy increase with increasing deposition temperature.

The $Tb_{26}Fe_{74}$ film samples studied here were dc magnetron cosputtered at substrate temperatures of $T_D = 77$, 300, and 525 K. The perpendicular magnetic-anisotropy energies range from 1×10^6 ergs/cm^3 for the $T_D = 77$ K sample, to 7×10^6 ergs/cm^3 for the $T_D = 525$ K sample. The intrinsic stress state for films deposited with an Ar gas pressure of 5 mTorr was found to be compressive[14] with the magnitude increasing with decreasing substrate temperature. A film deposited at 525 K using an Ar gas pressure of 10 mTorr resulted in a film having an intrinsic tensile stress. These results are qualitatively consistent with the work of Thornton and Hoffman.[15]

X-ray absorption spectra were collected using a total electron yield technique[16] at the Naval Research Laboratory's Materials Analysis beamline X23B (National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY). Data were collected using normal

and glancing angle (10° with respect to the film plane) incident radiation. Because the EXAFS signal originates with $\cos^2$ dependence with respect to the electric-field vector of the incident radiation these directions allow the sampling of in-plane and out-of-plane structure, respectively. EXAFS analysis procedures used here follow those presented in Ref. 17 leading to Fourier-transformed EXAFS data. To obtain a description of the near-neighbor environment an r-space range encompassing the near-neighbor Fourier peak was Fourier filtered to wave-vector space and fitted using calculated EXAFS data. The calculated EXAFS data were generated using the single-scattering, curved-wave EXAFS approximation of Rehr *et al.*[18] The uncertainty in the calculation of the electron phase shifts and amplitude reduction factors were improved by fitting to empirical standards of $TbFe_2$ and $TbFe_3$ powders. The analysis allows the calculation of the coordination number, radial distance, and Debye-Waller coefficients (thermal and structural disorder) of atomic shells around the absorbing species. The structural anisotropy discussed here is defined as the difference between the best fit parameters for the in-plane and out-of-plane data. As a consistency check we performed a similar analysis on the difference spectrum (out-of-plane EXAFS data subtracted from the in-plane EXAFS data) where the best fit describes the anisotropy directly.

Figures 1(a)–1(c) contain Fourier-transformed Fe EXAFS data for samples deposited at $T_D = 77$, 300, and 525 K, collected using normal and glancing incident radiation. These samples were all measured to be in compression.[14] The Fourier transform of EXAFS data is analogous to a partial radial distribution function where peaks in the spectrum typically correspond to the number and position of neighboring atoms. (It differs from the PRDF in that these data are not corrected for electron phase shifts, as a result the radial distances are shifted to lower values.) In Fig. 1 one sees an anisotropy between data sets for samples deposited at 300 and 525 K as a change in amplitude of the near-neighbor peak centered near 2 Å. No differences are seen in other regions of the transforms indicating that the anisotropy is highly localized and confined to the near-neighbor environment. Notice for the sample deposited at 525 K, the anisotropy is comparatively larger than that of the sample deposited at 300 K, with virtually no anisotropy seen in the amplitude of the near-neighbor peak region for the sample deposited at 77 K. These changes in structural anisotropy scale qualitatively with the magnetic anisotropy energy which increases monatomically with deposition temperature (see Fig. 2). Upon closer inspection one sees that the Fourier-transformed data corresponding to the sample deposited at 77 K illustrates a very different anisotropy. Unlike samples deposited at 300 and 525 K, the data corresponding to the sample deposited at 77 K illustrates a shift in the radial distance of the near-neighbor peak between the in-plane and out-of-plane structures suggesting that the atomic distances of the contributing atomic shells change between these directions.

A sample grown in tension at $T_D = 525$ K was also examined and found to have a similar structural anisotropy compared with that shown in Fig. 1(c), suggesting that the structural anisotropy in samples grown at elevated temperatures does not change appreciably with the intrinsic stress state of the film.

Figures 1(d)–1(f) are plots of the fitted data with the Fourier-filtered experimental data from Figs 1(a)–1(c). The radial distance, Debye-Waller coefficient, and coordination of each shell is floated during the fitting procedure. A summary of the fitting analysis presented in terms of changes in the local environment of Fe between the in-plane and out-of-plane structures is presented in Table I. The data shown in Fig. 1 as symbols are fitted using atomic shells of Fe at 2.47 and 2.65 Å, and Tb at 2.99 Å. In comparing the fitted to the experimental data there appears good agreement over the entire r-space range including the near-neighbor region showing the largest anisotropy. For samples deposited at 300 and 525 K the anisotropy arises from anisotropic pair correlations which manifest as a preference for Fe-Fe neighbors to align in plane and Fe-Tb neighbors to align out of plane. This structural anisotropy is qualitatively the same as that reported in Ref. 6. The amount of anisotropic pair correlations in the $T_D = 525$ K film are calculated to be $\approx 45\%$ greater than that measured in the $T_D = 300$ K film. In contrast, the data for the sample deposited at 77 K show no evidence of anisotropy in the local chemistry, but they do exhibit a significant shift of the near-neighbor peak. The structural anisotropy for this sample is therefore best described as an in-plane compression of the local environment. This in-plane compression is the result of the large stresses experienced during film growth via the sputtering of targets consisting of heavy elements.[15] The in-plane compression in the Fe-Fe near neighbors at 2.47 Å is measured to be $\approx 1.1\%$, with a corresponding $\approx 2\%$ compression in the Fe-Fe coordination shell at 2.65 Å. The Fe-Tb distance is also compressed in plane, but only 0.6%, which is close to the uncertainty associated with fitting of the Tb coordination shell ($\approx 0.5\%$). The calculation of the Debye-Waller factors for these coordination shells indicates that the out-of-plane structure is more disordered than the in-plane structure for this sample. Changes in radial distance and Debye-Waller coefficients were not found in samples deposited at 300 and 525 K, indicating the strain in these samples is below

TABLE I. Changes in the local environment around Fe atoms in $Tb_{26}Fe_{74}$ films determined via EXAFS fitting analysis. Data reflect changes between directions parallel and nearly perpendicular to the film plane. Difference errors represent a 20% change in goodness of fit for each orientation added in quadrature (Δ = parallel − perpendicular).

T_D (K)	Δr_{Fe} (Å)	ΔN_{Fe}	ΔN_{Tb}	K_u (10^6 ergs/cm^3)
77	−0.027±0.007	≤±0.2	≤±0.2	1.0
300	−0.01±0.007	0.8±0.2	−0.7±0.5	3.0
525	0.00±0.007	1.1±0.23	−1.0±0.5	7.0

the sensitivity of our experiment ($\leq 0.5\%$).

Figure 2 is a plot of the magnetic-anisotropy energy versus the amount of anisotropic pair correlations measured in samples deposited at increasing substrate temperatures. The degree of anisotropic pair correlations are presented as a percent difference between the in-plane and out-of-plane pairs divided by the average of the in-plane and out-of-plane pairs. The magnetic-anisotropy energy increases from 1×10^6 to 7×10^6 ergs/cm^3 across the range of deposition temperatures, 77 K $\leq T_D \leq$ 525 K, while the amount of anisotropic pair correlations increase from near 0% for the $T_D = 77$ K, to 11% for the $T_D = 525$ K sample. A similar relationship is found in the Fe-Tb correlations between the in-plane and out-of-plane structures. We find 1.0 ± 0.5 more Fe-Tb pairs along the direction perpendicular to the film plane in the sample deposited at 525 K. The changes in anisotropic pair correlations are roughly proportional to the changes in magnetic anisotropy with increasing deposition temperature.

The strong relationship between the magnetic and structural anisotropies in these samples as a function of substrate temperature suggests that a large part of the perpendicular magnetic anisotropy is associated with an atomic configuration where like pairs are favored in plane and unlike pairs perpendicular to the film plane. Presumably this anisotropic arrangement of atoms occurs during film growth where the deposition temperature determines

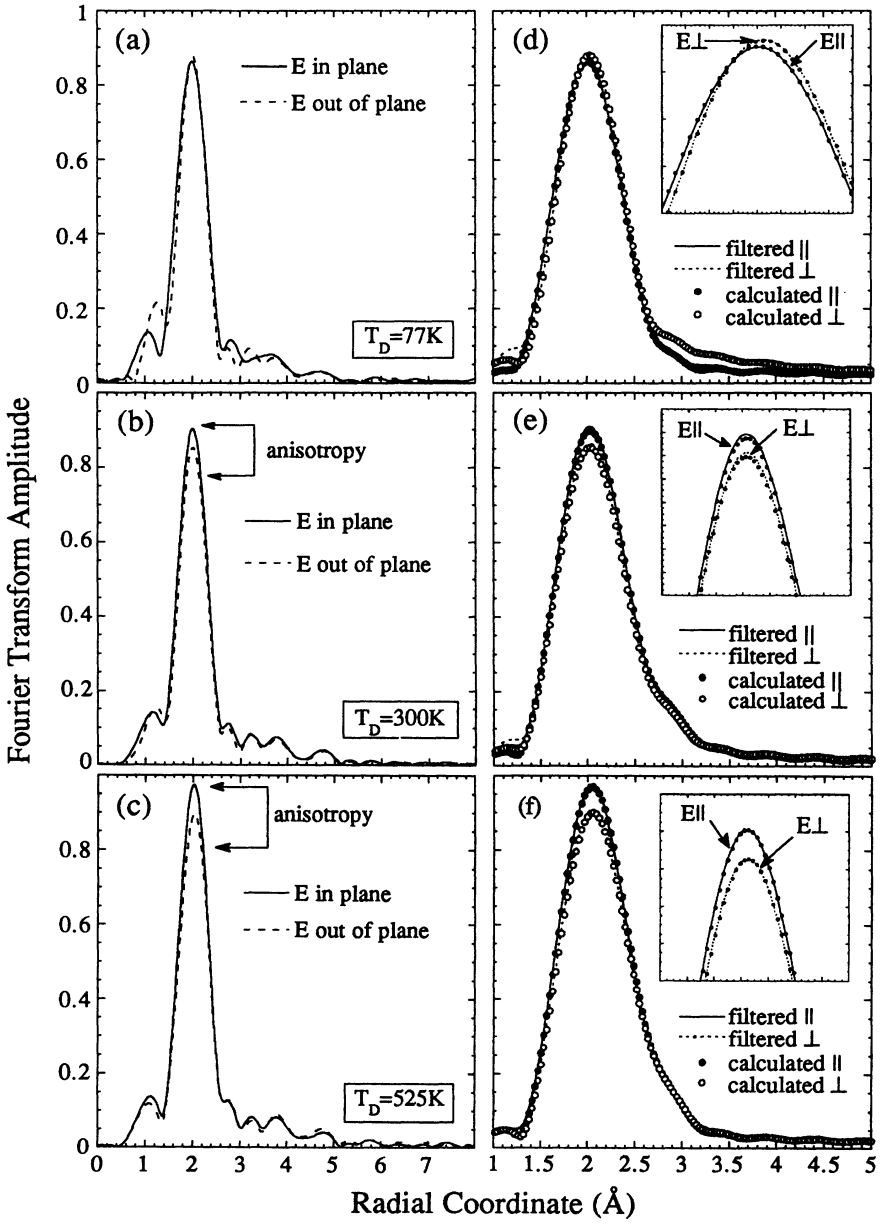

FIG. 1. Fourier-transformed Fe EXAFS data corresponding with the in-plane (——) and out-of-plane (— — —) structure for the three $Tb_{26}Fe_{74}$ films grown at (a) 77 K, (b) 300 K, and (c) 525 K. EXAFS data were Fourier transformed using identical k ranges of 2.3–9.75 Å^{-1} and k^2 weighting. The large peak centered near 2 Å in panels (a)–(c) was Fourier filtered using an r range of 1.5–3 Å and appears in panels (d)–(f) with calculated EXAFS data. ||: Electric-field vector oriented in the plane of the sample. ⊥: Electric-field vector oriented nearly perpendicular to the plane of the sample.

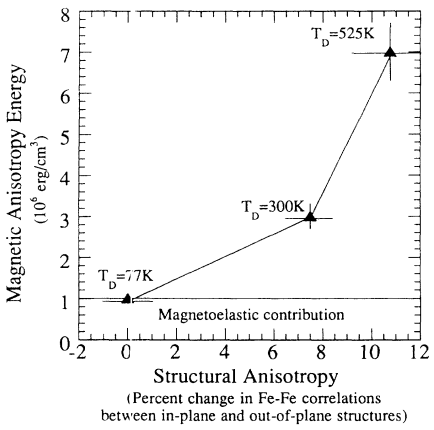

FIG. 2. Plot of magnetic anisotropy energy [after Hellman and Gyorgy (Ref. 11)] vs structural anisotropy. The deposition temperatures for each data point are listed in the figure. Error bars for the structural anisotropy are determined by a sensitivity analysis of the fitting parameters and maintain χ^2 to within 20% of the best fit. The error bars for the magnetic anisotropy represent a 10% experimental uncertainty.

the surface mobility of atoms and the degree to which they relax into energetically favorable sites. Subsequent layer growth acts to freeze the anisotropy into the bulk structure. The lack of anisotropic pair correlations in the samples deposited at 77 K indicates that the surface mobility during growth in this sample was too low to allow adatom site selection. This simple model accounts for both the trend of increasing anisotropic pair correlations with increasing deposition temperature and the lack of a local chemical anisotropy in the sample deposited at 77 K.

The strain in the 77 K film arises from compressive stresses which are commonly observed in sputtered films containing elements of high atomic mass.[15] These stresses are believed to be incorporated into the film during deposition by energetic Ar ions which are neutralized and reflected from the target impinging upon the substrate. By increasing the Ar gas pressure during deposition a film was grown at $T_D = 525$ K in a state of tension. Measurements performed on this sample exhibit anisotropic pair correlations similar to the sample grown in compression, indicating that the anisotropic pair correlations do not originate from a stress mechanism.

In conclusion, we suggest that in a-TbFe samples deposited at low temperatures, $T_D = 77$ K, the magnetic anisotropy is dominated by the magnetoelastic interaction between the film and substrate, while the magnetic anisotropy in samples deposited at temperatures ≥ 300 K is likely dominated by a crystal-field interaction on the Tb site through the coupling of its aspherical $4f$ charge cloud to an anisotropic electrostatic environment provided by the growth-induced anisotropic pair correlations.

These findings support the idea that the structural anisotropy in a-TbFe films is mainly growth induced and is responsible for most of the perpendicular magnetic anisotropy measured in these materials; a belief widely held since 1973.[1,7]

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