Magnetic properties of the $Co-C_{60}$ and $Fe-C_{60}$ nanocrystalline magnetic thin films

Lingyi A. Zheng^{a)} and Enrique V. Barrera

Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005

Robert D. Shull

Magnetic Materials Group, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8552

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The basic magnetic properties of $Co-C_{60}$ and $Fe-C_{60}$ nanocrystalline magnetic thin films and the temperature effects on these properties have been investigated. Experimental results show that the $Co-C_{60}$ films possess an in-plane magnetic anisotropy, but such an anisotropy is not found in the $Fe-C_{60}$ films. At room temperature, the magnetic coercivity decreases with increasing C_{60} concentration in the $Co-C_{60}$ films while it increases with increasing C_{60} concentration in the $Fe-C_{60}$ film. Strong temperature-dependent remanence and saturation magnetization are found in both the $Co-C_{60}$ and $Fe-C_{60}$ films with high C_{60} concentration due to the nanosize grain effects. The effects of temperature on the coercivity of the $Co-C_{60}$ and $Fe-C_{60}$ films are different and determined by the intrinsic magnetocrystalline anisotropy energy of Co and Fe, respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886271]

I. INTRODUCTION

Because of their advanced properties, nanomagnetic materials have had great impacts in the high-density magnetic storage media,¹ advanced soft magnetic materials,² and improved magnetocaloric materials.³ Since such advanced properties stem from the nanosize grain structures, nanomagnetic materials can be developed by manipulating the grain structure on the nanoscale by using various schemes. Adding fullerenes, such as C₆₀, to magnetic materials has, shown to be a promising method to engineer the nanostructures of the materials in our previous studies^{4,5} in which nanocrystalline metal- C_{60} magnetic thin films were made by thermal codeposition of ferromagnetic metals (Co, Fe, and CoFe) and fullerenes (C_{60}). Unique microstructures and promising magnetic properties have been observed in these films. Both are thought to be due to the formation of columnar nanosize grain structures with C₆₀ dispersed on the grain boundaries. Mass spectroanalysis and Raman scattering both show that the C_{60} molecules are stable in the films and interact strongly with the metallic matrix. X-ray diffraction patterns and transmission electron microscopy (TEM) analysis indicate that the crystal structures of the metallic grains are not altered by the addition of C₆₀, which means that the Co grains in the $Co-C_{60}$ film are hexagonal closed packed (hcp) and the Fe grains in the $Fe-C_{60}$ film are body centered cubic (bcc). A self-assembly grain growth mechanism has been proposed to explain the formation of the columnar grain structures in these films. Estimated grain sizes based on this mechanism agree with the experimental measurement and give a relationship between the grain size and the C_{60} concentration in these films. Kinetics grain growth study shows that these nanocrystalline metal-C₆₀ films have higher thermal stability than the pure metal films.⁵ All these microstructual results indicate that C_{60} has a dual function of forming and stabilizing the nanosize grains of the metal- C_{60} films. The grain structures versus C_{60} concentration relationship provide a practical guideline to modify the microstructures of these films. These preliminary findings indicate that these metal- C_{60} nanocrystalline thin films would have potential applications in many areas, such as high-density magnetic storage¹ and advanced soft magnetic material.² As a continuous study of the previous work, the basic magnetic properties of the nanocrystalline $Co-C_{60}$ and $Fe-C_{60}$ magnetic thin films and the temperature effects on these magnetic properties are investigated and reported in this article, providing the first hand magnetic characterization of the films.

II. EXPERIMENTAL PROCEDURE

A. In-plane magnetic properties at room temperature

The magnetic property measurements were performed in a Lakeshore⁶ vibrating-sample magnetometer (VSM) in National Institute of Standards and Technology (NIST). The sample was vibrated at a frequency of 30 Hz in a magnetic field generated by two coaxial coils in the X direction, and the induction current was detected by two pairs of pickup coils located in the X and Y directions shown in Fig. 1. In addition to being capable of measuring a conventional hysteresis loop, the customized VSM at NIST was also able to measure the in-plane magnetic anisotropy. The in-plane magnetic anisotropy measurement was accomplished by first placing the sample horizontally, parallel to the applied field, as shown in Fig. 1. The sample was then rotated by a stepping motor with a set angular interval. The saturation remanent magnetization (M_r) was thereby measured at multiple angular positions (θ) as the sample was sequentially rotated 360°. A M_r vs θ relationship was thus obtained and used to

^{a)}Present address: Micron Technology Inc., 9600 Godwin Drive, Manassas, VA 20110, U.S.A; electronic mail: lazheng@micron.com



FIG. 1. Sample setup for in-plane anisotropy measurement by VSM.

characterize the in-plane magnetic anisotropy of the film. $Co-C_{60}$ and $Fe-C_{60}$ films were chosen for study because Co and Fe are the two most important ferromagnetic elements. The Co-C₆₀ and Fe-C₆₀ thin films with different concentrations of C₆₀ molecules were fabricated by thermal vapor codeposition under ultrahigh vacuum ($<10^{-5}$ Pa). Highpurity (>99.999%, mass fraction) Co and Fe metallic sources and C₆₀ powder with purity of 99.95% were simultaneously evaporated from alumina-coated tungsten crucibles and condensed onto amorphous silicon-nitride-coated silicon wafers. Pure metallic Co and Fe films were also made at the same time under the same deposition conditions for comparison. All the films had a nominal thickness of 100 nm. The concentrations of carbon in the as-deposited thin films were measured by wavelength dispersive spectroscopy (WDS), and the resultant metal and carbon atomic fractions were converted to the ratio of the number of metallic atoms to the number of C_{60} molecules, expressed by the formula $M_x C_{60}$. The grain sizes in the as-deposited $Co-C_{60}$ and $Fe-C_{60}$ films with different C₆₀ concentrations were measured from plan view and cross-sectional TEM images in a JEOL 2000 transmission electron microscope. The TEM images were taken randomly for each sample and more than 300 grains were counted. The nominal diameter D, defined as the diameter of a circle with area equal to the measured grain area S, i.e., $D = \sqrt{4S/\pi}$, was used to describe the size of the grains in this study. The area of each grain was measured from the plan view TEM images using NIH IMAGE software. The arithmetic average of the nominal diameter D was used as the grain size of a film in this study. The VSM samples were cut from the substrate with dimensions of about 4×4 mm². The sample was mounted on the flat end of the sample holder and aligned parallel to the magnetic field. All the samples were tested for in-plane anisotropy first with the method described above. For the samples having in-plane anisotropy, a major hysteresis loop was measured in the positions at which both the maximum and minimum saturation magnetizations were found.

B. Magnetic properties at low temperatures

The magnetic properties of the materials are temperature dependent. Due to their nanograin structures and nanoscale magnetic domains, the magnetic properties of nanomagnetic materials are even more sensitive to temperature. Information about the magnetic structure and interaction in the nano-



FIG. 2. In-plane magnetic anisotropy in the Co–C₆₀ films at 298 K: (a) M_r vs θ and (b) M vs H hysteresis loops at different angular positions.

crystalline C₆₀-Metal films can be extracted from the study of the temperature effects on the magnetic properties in these films. To do this, the major magnetic hysteresis loops at low temperatures (4, 5, 50, 100, 150, 200, 250, and 298 K) were measured in a superconducting quantum interference device (SQUID) magnetometer using liquid helium as the coolant. The samples were of dimension of about 4×4 mm² and mounted to the sample holder with the thin-film surface parallel to the magnetic field.

III. RESULTS AND DISCUSSIONS

A. In-plane magnetic anisotropy

In-plane magnetic anisotropy was found in the high C_{60} concentrated $Co-C_{60}$ magnetic films. The remanent magnetization $M_r(\theta)$ at different θ positions using the procedure delineated in Sec. II was measured. Each measured $M_r(\theta)$ value was normalized to the average value of $M_r(\theta)$, and at the ratio of $M_r(\theta)/M_r$ (average) is plotted against θ in Fig. 2. Periodic variation of M_r is obviously seen in the $Co_{162}C_{60}$ and $Co_{50}C_{60}$ films which have a high concentration of C_{60} molecules. The θ position having the highest M_r value indicates the direction of easy magnetization, while the θ position with the lowest M_r value points out the hard magnetization direction. It is interesting that the highest and lowest of M_r values are found at positions about 90° apart, implying a



FIG. 3. Normalized in-plane remanence measurements for the Fe– C_{60} samples at 298 K showing no in-plane magnetic anisotropy in these films.

uniaxial anisotropy. The magnetic hysteresis loops of these samples were measured at two positions: one with H aligned along the easy magnetization axis and the other with the field along the hard axis. The different shapes of these two loops are as expected with square and elongated loops along the easy and hard directions, respectively. However, the in-plane magnetic anisotropy was not found in the $Fe-C_{60}$ films as the remanent magnetization was hardly position (angle) dependent in the rotational remanence measurement for various $Fe-C_{60}$ films shown in Fig. 3. As no in-plane preferred crystallographic orientation was originally expected in these films using the current deposition methods and substrates, the most likely cause of the observed anisotropy is magnetostriction in the film due to a residual uniaxial stress resulting from the combination of thermal stress created in the film deposition process as well as the presence of the large C_{60} molecules embedded in the film. During deposition, the temperature of the substrate can be much higher than room temperature due to the radiation from the heated source crucibles and the heat from the metal vapors. As only one part of the substrate was exposed to the window at a time, the temperature of the substrate might not be uniform, thereby giving rise to a uniaxial stress when the substrate and film cooled to room temperature after deposition. The addition of the C_{60} molecules intensifies the stress in the film as it increases the mismatch of thermal-expansion coefficients of the film and the substrate. The higher the C₆₀ concentration, the higher the stress, and the higher the anisotropy. Our suspect that the magnetic anisotropy in the $Co-C_{60}$ films but not in the Fe-C₆₀ films was induced by magnetostriction is consistent with the fact that Fe has a much smaller magnetostriction coefficients λ_s (-7×10⁻⁶) than Co (-30×10⁻⁶).⁷ As the anisotropy constant K_{σ} induced by stress (σ) is equal to $3/2\lambda_s\sigma$, a smaller λ_s results in a smaller magnetostriction effect for the same stress level.

B. Magnetic coercivity at room temperature

The magnetic coercivity can be obtained from the hysteresis loop measurement. It is found that the coercivity of the $Co-C_{60}$ films decreases with increasing C_{60} concentration, as shown in Fig. 4. Although our previously published grain growth mechanism and TEM images indicated that the C_{60} molecules were located at the Co grain boundaries, the



FIG. 4. In-plane coercivity in the Co $-C_{60}$ films vs concentration of C_{60} molecules at 298 K.

coercivity data would seem to indicate that the C_{60} molecules do not retard very much the motion of domain walls in the material. Although it is not clear whether or not the domainwall movement is the principal factor controlling the coercivity in these Co- C_{60} films, comparison of the domain-wall width to the size of the C_{60} molecule is helpful in clarifying the issue. The width of a 180° domain wall can be calculated as follows:⁸

$$\delta = \pi \left(\frac{A}{K}\right)^{1/2} = \pi \left(\frac{kT_c}{aK}\right)^{1/2},\tag{1}$$

where *A* is the exchange energy parameter (or exchange stiffness), *K* is the magnetocrystalline anisotropy constant, *k* is Boltzmann's constant $(1.38 \times 10^{-23} \text{ J/K})$, *T_C* is the Curie temperature, and *a* is the lattice spacing.

The domain-wall thicknesses δ for Co and Fe are calculated and listed in Table I.

The domain-wall widths for Co and Fe are both much larger than the size of a single C_{60} molecule (1 nm), the size of a small cluster of C_{60} molecules (2–5 nm), and the grain sizes (3–10 nm) in these thin films. According to the common knowledge,⁸ a domain wall is not expected to interact very strongly with an inclusion, second phase, or crystallographic defect that is either much narrower or much wider than itself. Therefore, it is reasonable to conclude that the nanoscale dispersion of C_{60} molecules would not have strong effects on pinning domain movement in Co.

Contrary to the behavior of the Co–C₆₀ films, the magnetic coercivity of the Fe–C₆₀ films increases with increasing C₆₀ concentration (Fig. 5). For illustration, the hysteresis loops for pure Fe and Fe₁₄₉C₆₀ are plotted in Figs. 6 and 7, respectively. For the pure Fe sample, a very square hysteresis loop $(M_r/M_s=0.92)$ was observed. Single-crystal Fe has

TABLE I. Magnetic properties and domain-wall thicknesses of Co and Fe.

Parameters	Со	Fe
a (nm)	0.25	0.286
T_c (K) (Ref. 9)	1394	1043
$K (J/m^3)$ (Ref. 9)	4.1×10^{5}	4.2×10^{4}
A (J/m)	7.69×10^{-11}	5.03×10^{-11}
$(A/K)^{1/2}$ (nm)	13.7	34.6
Domain wall δ (nm)	43.0	108.7



FIG. 5. In-plane coercivity in the $\rm Fe-C_{60}$ films vs concentration of $\rm C_{60}$ molecules at 298 K.

three different magnetocrystalline anisotropy axes: [100], [110], and [111].⁹ The easy axis is the [100] direction with a saturation field of about 5.6 kA/m [70 Oe, i.e., $70/4\pi$ (kA/m)]. The saturation fields for the [111] and [110] directions are about 35.8 kA/m [450 Oe, i.e., $450/4\pi$ (kA/m) and 43.8 kA/m [550 Oe, i.e., 550/4 π (kA/m)], respectively. Since a random grain structure is observed in the pure iron sample, a low M_r/M_s ratio would be expected, as the magnetization vector in those grains with [111] and [110] axes along the applied field direction will rotate back to the [100] direction after the external field is removed. However, it is also found that the grain size of this sample is about 15 nm which is less than the ferromagnetic exchange length $L_{\text{ex}} = (A/K)^{1/2} = 34.6$ nm in Fe (refer to Table I). According to the modified random anisotropy (RA) model proposed by Herzer,¹⁰ the effective anisotropy constant $\langle K \rangle$ is the value averaged over all the grains within the range of the exchange distance. $\langle K \rangle = K / \sqrt{N} = K (D/L_{ex})^{3/2}$ when the grain diameter D is smaller than the exchange length L_{ex} . In the pure Fe film, the grains are also likely to be small and continuous so that ferromagnetic exchange interactions extend past the grain boundaries. Therefore, this film's anisotropy constant would be reduced to $K(D/L_{ex})^{3/2}=0.285K$. Since the saturation fields along the hard axes [111] and [110] directions are the fields required to overcome the magnetocrystalline anisotropy, the reduction in the magnetocrystalline anisotropy constant should correspondingly result in a reduction in the



FIG. 6. Magnetization vs field measurements at 298 K for a pure Fe thin-film sample.



FIG. 7. Magnetization vs field measurements at 298 K for an $Fe_{147}C_{60}$ thin-film sample.

saturation field by the same factor. This would reduce the saturation fields to 10.2 kA/m [128 Oe, i.e., $128/4\pi$ (kA/m)] and 12.5 kA/m [157 Oe, i.e., $157/4\pi$ (kA/m)] in the [111] and [110] directions, respectively.

Despite the fact that the predicted M_s value for the pure Fe film matches the experimental results (Fig. 6), it is apparent that the RA model does not apply to the Fe-C₆₀ films because the strong ferromagnetic exchange interaction between Fe grains is prevented by the isolation effect of the dispersed C₆₀ molecules between them based on the microstructual observation and the following reasoning. For these



FIG. 8. Calculated superparamagnetic relaxation time for isolated columnar Fe grains with different grain sizes at the indicated temperatures where the height of the columnar grain has been taken to be (a) 100 nm and (b) 50 nm. Only room-temperature data are shown for Co.

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films, a low M_r/M_s ratio and high saturation field are measured. The grain sizes in the Fe₁₄₇C₆₀ and Fe₈₃C₆₀ films are about 8 and 5 nm, respectively. These are much smaller than the grain size in the pure Fe film and the exchange length of Fe. If the RA model was valid in this system, the saturation field of these two C₆₀-containing samples should be less than that of the pure Fe film of 10.2 kA/m [128 Oe, i.e., 128/4 π (kA/m)]. Instead, in the Fe₈₃C₆₀ film (Fig. 9), the saturation field is about 39.8 kA/m [500 Oe, i.e., 500/4 π (kA/m)], a value very close to the saturation field of single-crystal iron in the [111] direction.

C. Superparamagnetism and effects of temperature on the magnetic properties

In Sec. III B, it was shown that the strong magnetic exchange among the nanosize grains was prevented by the isolation effects of the dispersed C_{60} , resulting in the invalidity of the RA model in this nanocrystalline magnetic films. However, if the nanosize grains are completely isolated and form single magnetic domains in each individual grain, superparamagnetism would take place. In that case (i.e., that of a single domain particle with uniaxial anisotropy), the magnetic energy can be expressed as¹¹

$$E = KV \sin^2 \theta, \tag{2}$$

where *K* is the magnetic anisotropy energy constant, *V* is the volume of the particle, and θ is the angle between the magnetization direction and an easy direction of magnetization. Equation (2) shows that there are two energy minima at $\theta = 0^{\circ}$ and $\theta = 180^{\circ}$ which are separated by an energy barrier of magnitude *KV*. For very small particles the energy barrier may be comparable to or smaller than the thermal energy, even at temperatures below room temperature. This results in the relaxation of magnetic spin directions in the superparamagnetic state (i.e., spontaneous fluctuations of the magnetization direction between the $\theta = 0^{\circ}$ and $\theta = 180^{\circ}$ states). The superparamagnetic relaxation time τ is given by the following:

$$\tau = \tau_0 \exp\left(\frac{KV}{kT}\right) = \tau_0 \exp\left(\frac{K}{kT}\frac{\pi D^2 h}{4}\right),\tag{3}$$

where τ_0 is a constant of the order of $10^{-10}-10^{-13}$ s, k is the Boltzman's constant, and T is the temperature in kelvin. In the following calculations, we will use the intermediate value of 10^{-11} s for τ_0 .

Based on Eq. (3), the relaxation time for the Fe-C₆₀ films can be calculated under the assumption that the cylinder-shaped grains have a diameter of D and a height of h under different temperature conditions. The results are shown in Fig. 8 with h equal to either the thickness of the film (100 nm) or half the thickness of the film (50 nm). It is clearly seen that at room temperature the relaxation time for Fe with grain size around 5 nm is less than 1 s at both thicknesses, strongly suggesting the presence of superparamagnetic behavior and the loss of ferromagnetism (no remanence). However, since remanence and hysteresis behavior is still observed in this film, it is unlikely that all the grains in these films are completely isolated and form single domains.



FIG. 9. Major M vs H hysteresis loops for the Fe₈₃C₆₀ thin-film sample measured at the indicated temperatures (a) in the complete field range of measurements and (b) magnified plot in the low-field region.

The above calculation also shows the significant impact of temperature on materials with a low magnetocrystalline constant (K), such as Fe, when they have nanoscale grains. Cobalt, on the other hand, has a K about ten times larger than that for Fe and is therefore not likely to develop superparamagnetic behavior under these same conditions. The ideal superparamagnetic relaxation time was calculated assuming completely isolated single domain entities. The observed deviation from the ideal model in the experimental nanocrystalline films implies an interaction of neighboring grains and the formation of large domains in these films. For grains (each possessing the critical size for being a single magnetic domain) in an assembly, such as a continuous film, the relaxation time provides a measure of the grain-grain magnetic interaction. Since the relaxation time is strongly temperature dependent, an investigation of the temperature dependence of M will give insight to the understanding of these nanocrystalline materials.

Figure 9(a) shows the major loops of the $Fe_{83}C_{60}$ film measured by SQUID at different temperatures with the magnetic field *H* parallel to the film plane. The low-field region



FIG. 10. Major M vs H hysteresis loops for the Fe₁₄₇C₆₀ thin-film sample measured at the indicated temperatures (a) in the complete field range of measurements and (b) magnified plot in the low-field region.

is magnified and plotted in Fig. 9(b). Both the magnetization remanence M_r and saturation M_s are found to change strongly with temperature. The same tendency is found in the $Fe_{147}C_{60}$ film (Fig. 10) but not in the pure Fe sample (Fig. 11). In order to compare the temperature effects of different samples, the values (M_r, M_s) at temperature T are normalized to their values at room temperature (298 K). Two parameters $R_{mr}(T) = M_r(T) / M_r(298)$ and $R_{ms}(T) = M_s(T) / M_s(298)$ are introduced to describe these effects. The relationships of R_{rm} vs T and R_{sm} vs T are plotted in Fig. 12. The temperature effect is clearly seen and closely related to the C60 concentration in the films. R_{rm} has a nearly linear relationship to T with an increasing slope as the C60 concentration increased. The linear fits of the data gave the functions $R_{rm} = (1.26/8.5)$ $\times 10^{-4}$ T and $R_{rm} = (1.17 - 5.5) \times 10^{-4}$ T for the Fe₈₃C₆₀ and Fe147C60 samples, respectively. These fits show that about 26% and 17% of the M_r , respectively, vanished in these two materials when the temperature was raised from 5 K to room temperature. These are notable changes when compared to the nearly constant (1% change) M_r of the pure Fe sample over the same temperature range. Simultaneously, the saturation magnetization increased by only 6% and 5%, respectively, in the $Fe_{83}C_{60}$ and the $Fe_{147}C_{60}$ films and by less than 1% in the pure Fe film. Conventionally, the difference between M_s and M_r accounts for the reversible magnetization due to the rotation of magnetization vectors whose easy axes are not aligned in the applied field direction. Since Fe has a



FIG. 11. Major M vs H hysteresis loops for the pure Fe thin-film sample measured at the indicated temperatures (a) in the complete field range of measurements and (b) magnified plot in the low-field region.

Curie temperature of 1043 K, M_r and M_s are not expected to be sensitive functions of *T* at temperatures below room temperature in bulk materials with large grains. The strong temperature dependence observed in the Fe–C₆₀ films is therefore attributed to the nanometer grain-size effect in the samples. With average grain sizes of 5 and 8 nm in the Fe₈₃C₆₀ and the Fe₁₄₇C₆₀ films, respectively, superparamagnetism is calculated (Fig. 8) to occur even at room temperature. Since the grains are not ideally separated, ferromagnetism still dominates the overall behavior. However,



FIG. 12. Normalized saturation and remanent magnetization vs temperature data for the $Fe-C_{60}$ films showing strong temperature effects in the films with high concentrations of C_{60} molecules.



FIG. 13. Major M vs H hysteresis loops for the Co₅₀C₆₀ thin-film sample measured at the indicated temperatures showing the variation of M_r and M_s with temperature.

because the grain sizes have a statistical distribution and the grains are isolated by C₆₀ on the grain boundaries, formation of magnetic domains with sizes below the critical size for superparamagnetism is possible. These small domains can be within one grain or encompass a cluster of grains, and the chance of forming them is greater in these materials with smaller grain size. This is the reason for the larger reduction of remanence in the Fe₈₃C₆₀ sample with temperature than in the other samples which are more dilute in C_{60} . M_s is considered to be an intrinsic property of the ferromagnetic material. Therefore, it is not surprising to find it to be nearly a constant with temperature for the pure Fe sample. The increase in M_s at low temperatures in the Fe-C₆₀ films may be attributed to the large grain-boundary volume where atoms have different spacings. However, the increase in M_s on decreasing T from 298 to 5 K is less than that for M_r . This result is consistent with the existence of superparamagnetism explanation because the measurement of M_s occurs in the presence of an external applied field which is sufficiently large to prevent the random fluctuation of spins away from that direction by thermal excitation, thereby subduing the superparamagnetic relaxation phenomenon.

Similar results were observed in the high C_{60} molecule concentration Co-C₆₀ samples. Figure 13 shows the hysteresis loops measured for the Co₅₀C₆₀ sample at different temperatures. The relationships of R_{rm} vs T and R_{sm} vs T are plotted in Fig. 14. The temperature effects are clearly seen and closely related to the concentration of the C_{60} molecules. Due to the very high C_{60} concentration (55 atomic fraction of carbon) in this sample, the grain size in this film is about 4 nm and the film has a honeycomblike structure with the core Co grains surrounded by the C_{60} molecules. Although Co has a high magnetocrystalline anisotropy constant K, it is still possible that grains with 4-nm size may possess superparamagnetic behavior at room temperature. In the calculations presented in Fig. 8, it was assumed that all the grains have a height equal to either the thickness (100 nm) or half the thickness (50 nm) of the film. However, the heights of the grains also have a statistical distribution in size just as does the grain diameter. Therefore, it is helpful to look into how grain height can change the superparamagnetic relax-



FIG. 14. Normalized saturation and remanent magnetization vs temperature data for the $Co-C_{60}$ films showing strong temperature effects in the films with high concentrations of C_{60} molecules.

ation time for grains with a diameter of 4 nm (the average grain size of $Co_{50}C_{60}$) and 11 nm (the average grain size of $Co_{162}C_{60}$). The calculated results are shown in Fig. 15. For the grains with the diameter of 4 nm, the relaxation time is less than 1 h when the grain height is shorter than 25 nm, i.e., a quarter of the film thickness. For any reasonable distribution function, there should be a fraction of grains with height within this range. For the grains with the diameter of 11 nm, the grain height has to be below 3 nm in order to show superparamagnetic behavior below 298 K. One can expect that the number of grains with height below 3 nm would be very low. Based on this analysis, it is reasonable that M_r and M_s of the Co₅₀C₆₀ film with grain size of 40 Å should have a much stronger temperature dependence than the other Co films with large grain sizes. The comparison of the experimental results among these films is shown in Fig. 16 and the results are consistent with the superparamagnetic relaxation-time calculations.

A normalized factor $R_{H_c} = H_c(T)/H_c(298)$ is introduced to compare the temperature effects on the magnetic coercivity (H_c). Figure 16 shows the R_{H_c} vs *T* curves for different samples. Here, it is found that the Co-C₆₀ films have stronger temperature dependencies than the Fe-C₆₀ films. In the Co-C₆₀ films, the higher the C₆₀ concentration, the stronger the effect. H_c increases with decreasing temperature except



FIG. 15. Calculated superparamagnetic relaxation time vs grain height at room temperature for the columnar Co grains with the diameters of 4 and 11 nm.



FIG. 16. Normalized coercivity vs temperature relationships for the samples investigated here showing strong temperature effects on the coercivity of the $Co-C_{60}$ films and weak effects on the coercivity of the $Fe-C_{60}$ films.

between 4 and 50 K for the $Co_{162}C_{60}$ sample. The $Co_{162}C_{60}$ measurements at 4 and 50 K were repeated with similar results, so the decrease in H_c for decreasing T from 50 to 4 K in this sample is considered to be a real effect. Compared to the $Co-C_{60}$ films, both the pure Co and Fe films have a lower but nearly linear H_c increment with decreasing temperature. In the $\mathrm{Fe-C}_{60}$ films, the temperature effects are weaker than in the pure Fe and the pure Co films. The different responses of the coercivity to the temperature in the $Co-C_{60}$ films and the Fe-C₆₀ films lead us to consider other origins of coercivity in addition to the grain-size effects, such as variations in the magnetocrystalline anisotropy energies. Figure 17 shows the magnetocrystalline anisotropy constant (K) of Co and Fe at different temperatures.^{12,13} For Co, K increases about 100% from room temperature to -196 °C (80 K) while K for Fe is nearly constant. The fact that Co has a stronger temperature-dependent anisotropy constant than Fe explains the different behaviors of the coercivity in these two systems. An increase of K will boost the coercivity no matter whether the coercivity derives from domain nucleation, movement, or rotation effects. In the case of the domain nucleation and movement, increasing K will decrease the domain-wall width $\delta[=(A/K)^{1/2}]$, resulting in the pinning effects by smaller inclusions and defects. In the domain rotation case, the enhancement of K increases the energy needed to change the magnetization moment direction. That the difference in the T dependence of the coercivities in the Fe-C₆₀ and Co-C₆₀ samples due to variations in K is consistent with the observed T dependence of the saturation field in these systems. Close examination of the hysteresis loops in the $Fe-C_{60}$ samples shows that the saturation fields are almost the same for all temperatures, while the saturation moments are different. In contrast, the saturation field increases with decreasing temperature in the $Co-C_{60}$ films. All these are related to the change in the anisotropy energy with temperature.

It is therefore concluded that the temperature effects on M_r and M_s are attributed to the nanosize grains while the effects on H_c stem from the magnetocrystalline anisotropy energy variations in these metal-C₆₀ nanostructured magnetic thin films.



FIG. 17. Magnetocrystalline anisotropy constant (K) at various temperatures for (a) Co and (b) Fe metals (see Refs. 12 and 13).

IV. CONCLUSIONS

The basic magnetic properties of the $Co-C_{60}$ and Fe-C₆₀ nanocrystalline magnetic thin films and the temperature effects on these properties have been investigated. The experimental results show that the Co-C₆₀ films have inplane magnetic anisotropy and that the anisotropy increases with increasing C_{60} concentration. On the contrary, the $Fe-C_{60}$ films do not show in-plane magnetic anisotropy. The difference in the anisotropy behavior between the $Co-C_{60}$ and $Fe-C_{60}$ films is likely due to the high magnetostriction coefficient of Co and the low coefficient of Fe. At room temperature, the magnetic coercivity decreases with increasing C_{60} concentration in the Co- C_{60} films while it increases with increasing C_{60} concentration in the Fe- C_{60} film. The temperature-dependent relationship of the magnetization remanence in the $Co-C_{60}$ and $Fe-C_{60}$ films increases strongly with increasing C₆₀ concentration. The remanence increases sharply in high C₆₀ concentration films due to the large superparamagnetic effects from the nanosize grains in these films. Temperature has a strong effect on the coercivity of the $Co-C_{60}$ films and a weak effect on the coercivity of the $Fe-C_{60}$ films. This effect is consistent with the temperature effect on the intrinsic magnetocrystalline anisotropy energy of Co and Fe.

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¹E. S. Murdock, R. F. Simmon, and R. Davision, IEEE Trans. Magn. **28**, 3078 (1992).

²G. Herzer, J. Magn. Magn. Mater. **112**, 258 (1992).

³R. D. Shull, R. D. McMichael, and J. J. Ritter, Nanostruct. Mater. **2**, 205 (1993).

⁴L. A. Zheng, B. M. Lairson, E. V. Barrera, and R. D. Shull, Appl. Phys. Lett. **77**, 3242 (2000).

⁵L. A. Zheng, E. V. Barrera, and R. D. Shull, J. Appl. Phys. **92**, 523 (2002). ⁶Equipment manufacturers are only used here to properly describe the experimental conditions of the study and is not intended to imply a recommendation or endorsement by the National Institute of Standards and Technology.

⁷R. S. Tebble and D. J. Craik, *Magnetic Materials* (Wiley-Interscience,

New York, 1969), p. 30.

⁸R. A. McCurrie, *Ferromagnetic Materials Structure and Properties* (Academic, New York, 1994), p. 15.

- ⁹Centre D'Information Du Cobalt, *Cobalt Monograph* (Battle Meomrial Insitute, 1960), p. 98.
- ¹⁰G. Herzer, IEEE Trans. Magn. **26**, 1398, (1990).
- ¹¹S. Morup, in *Nanomagnetism*, edited by A. Hernando (Kluwer Academic Publishers, Dordrecht, 1993), p. 93–99.
- ¹²Centre D'Information Du Cobalt, *Cobalt Monograph* (Battle Meomiral Insitute, 1960), p. 100.
- ¹³R. S. Tebble and D. J. Craik, *Magnetic Materials* (Wiley-Interscience, New York, 1969), p. 64.