The 3rd MINT G8 Workshop

Abstract

“High Performance Permanent Magnets Sustainable for Next Generation”
(NSF-CMMI 1229049)

June 5, 2015
The Third MINT G8 Workshop
(June 5, 2015)
Bevill 1000

Schedule

1. 1:15 – 1:25: Remarks by Associate VP for R.& E.D. Allen Parrish

2. 1:25 – 1:40: T. Suzuki (Overview)


4. 2:00 – 2:10: S. Zhao, T. Hozumi, P. LeClair, G. Mankey and T. Suzuki; “Magnetic Anisotropy of τ-MnAl Thin Films”


10. 3:40 – 4:00: P. Visscher; “Dynamic instability mechanisms for switching hard grains

11. 4:00 – 4:20: J. Green, A. Chaturvedi, R. Schad, T. Suzuki; “Analysis of Interface Mixing and Alloy Formation of Rh/Mn Superlattices upon Annealing using XRD Reflectivity and Diffuse Scattering”


13. 4:40 - 5:00 Wrap up

5:00 pm Adjourn
Overview

Takao Suzuki

Background: Permanent magnets (PMs) are key for many applications including electric devices, motors, and actuators. The PMs with the highest known energy products (called (BH)max) are NdFeB magnets with (BH)max of about 50MGOe. The annual increase in NdFeB production has been more than 10% in the past decade and is expected to increase. However, more than 95% of current production capacity for rare-earth elements (REE) is in China, and thus this creates risks for global markets. Also, rare earth extraction processes lead to serious environmental problems.

Since there is no fundamental reason why non-REE magnets cannot have a high energy product, it is a high priority to develop “REE free” high energy-product PMs. The present proposal focuses on the issue of PMs in view of “Replacement of Scarce and Expensive Elements, Critical for Energy Applications”.

Objective: The proposed consortium intends at the first stage to develop REE free PMs of thin films and particles by better understanding the fundamental physics of the coercivity mechanism and the energy product, for applications such as magnetic MEMS biomedical sensors. For this purpose, the Mn alloy systems, such as Mn-Al, Mn-Bi, Mn-Ga and their ternary and quaternary alloys are the choice of materials. The advantages of such Mn-Alloy systems are that they exhibit high magnetic anisotropy and high coercivity, potential for high (BH)max. and that Mn and Al are abundant, thus providing a useful context to establish a cost-effective and sustainable manufacturing process. At the second stage, emphasis will be placed on the development from thin films and particles to powders and bulk PMs. The performance goal is to achieve (BH)max, comparable to NdFeB (50 MGOe). Also, the development of fabrication processes for production and recycling of the materials will be integrated with the aid of an industry expert, the aforementioned unfunded member of TDK.

Procedures: The activity consists of i) PMs fabrications, characterization and analyses, ii) Theoretical approaches and iii) Production and recycling of materials resources.

Organization: The consortium consists of five organizations from three countries. The MINT Center at Univ. Alabama is the principal institution. The partner institutions are Univ. of Delaware (USA), National Institute for Materials Science (NIMS, Japan), Max Planck Institute (Germany, MPI) and Technical University of Darmstadt (Germany). In addition, there is an industry participant (TDK, Japan) as a non-funded member. Its role is to discuss manufacturing processes, provide expertise on the materials supply chain from extraction, processing, and required components to end-use technologies.

The G8 MINT team consists of the 12 faculty members, a few graduate students and postdoctoral fellows.

Activities:

i. Mutual Collaborations
ii. Disseminations (Publications, Presentations, Patents)
iii. International G8 Workshop (Annual)
iv. MINT G8 Workshop (Annual)
v. Annual Report (National Councils)
vi. Newsletters
vii. Website
viii. Consortium Agreements
Investigation into Magnetic Anisotropy of Low Temperature Phase (LTP) MnBi Thin Films

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The temperature dependence of magnetic anisotropy in the LTP MnBi thin films is discussed in conjunction with saturation magnetization and lattice constants. It is experimentally found that $K_u$ is inversely proportional to the 8th power of the saturation magnetization $M_s$. It is also found that the $K_u$ is proportional to the unit cell volume. The calculation based on first principles of magnetic anisotropy energy as function of lattice constants (a and c) and statistical simulations of its spin temperature dependence is consistent with the experimental results. However, the spin reorientation transition taking place at 100K is not accounted for by the present calculation.

Index Terms – Low temperature phase MnBi, Magnetic anisotropy, Lattice constant, Rare-earth free magnet.

I. INTRODUCTION

There has been a growing interest in thin films and nano-particles of permanent magnets for various applications including MEMS [1] and biomedical applications [2]. Among many possible candidates, the manganese-based alloys such as MnBi and MnAl are attractive because their abundance, allowing a cost-effective and sustainable manufacturing process, in addition to their high magnetic anisotropy of the order of the 10^7 erg/cc at room temperature. Among many Mn-alloy based magnets, the low temperature phase (LTP) MnBi is known to exhibit the unique temperature dependence of a magnetic anisotropy constant $K$ which increases with temperature $T$ from about 100K to 500K, reaching to about 5x10^7 erg/cc at 500K [3]-[6]. This behavior of the increase in $K$ with $T$ is very attractive not only for basic studies of the origin of the magnetic anisotropy, but also for applications for devices operated at an elevated temperature. Further, it was pointed out [3] that the magnetostriction constants of the LTP MnBi alloy show an interesting behavior with temperature, which was suggested to be correlated with the magnetic anisotropy behavior.

In contrast to much experimental work, there has been little theoretical understanding of this interesting behavior of the magnetic anisotropy with temperature in LTP MnBi. A theoretical work based on first principle calculations showed that the magnetic anisotropy constants of LTP MnBi strongly depended on the unit cell volume [7]. It was also suggested the $K_u$ is strongly dependent on the number of valence electrons, hinting a further increase in $K_u$ by substituting Bi by another element such as Sn [7]. Further, a recent calculation [8] showed a strong correlation of the lattice constant with the magnetic anisotropy energy of the LTP MnBi. However, the experimental results are at variance with this calculation, which requires a significant adjustment to match the reported data. The present study has been carried out to elucidate the mechanism for its temperature dependence of LTP MnBi thin films from both experiment and theory.

II. EXPERIMENTAL

Multilayers of [Mn (x nm) / Bi (y nm)] x N were fabricated onto silica glass by sputter-deposition, where $x = 2.0$, $y = 1.1 \sim 7.9$ and $N = 1 \sim 10$. The deposition rates for Bi and Mn were 0.07 nm/s and 0.02 nm/s, respectively. The samples were deposited at an ambient temperature and were subsequently annealed in vacuum at various temperatures $T_a$ from around 300°C to 550°C for annealing times $t_a$. The thicknesses of each Bi and Mn layer were chosen to be 3.2 nm and 2.0 nm, respectively. The crystal structure of the films thus fabricated was characterized by X-ray diffraction with Co and Cu Kα radiation and also by high resolution electron microscopy. Measurements of the temperature dependence of magnetic properties were carried out.
using a vibrating sample magnetometer in fields up to 9T over a temperature range from 4K to about 400K. Torque magnetometer measurements were carried out for the out-of-plane mode in fields up to 9T over the temperature range mentioned above.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern obtained with the Co Kα for the MnBi thin film with $x=2$, $y=3.2$, $N=10$, $T_a=550$ °C and $t_a=0.5$hr. It is clearly seen that the sample is identified to be of the LTP phase with a preferential orientation of the c-axis along the film normal, although there are some other orientations present. High resolution TEM revealed that the sample consists of the LTP phase grains of about 10~100 nm surrounded by Mn and Bi which are mostly of amorphous, as already reported elsewhere [9]. Those amorphous phases, which are not evident by XRF, are also found to be nearly the same size of the LTP phases. It was, therefore, concluded in the previous work that high coercivity of about 15~20 kOe, which is about 1/3~1/2 of the magnetic anisotropy field, results from a single domain behavior. This conclusion was supported by the result of the so-called $\delta$-M curve measurements [9].

![Fig.1 The XRD pattern for the LTP MnBi thin film with $x=2$, $y=3.2$, $N=10$, $T_a=550$ °C and $t_a=0.5$hr. (Co Kα).](image1)

Figure 2 shows the lattice constant $c$ with measurement temperature over a temperature range from 300 to 550K for the c-axis oriented sample mentioned above ($x=2$, $y=3.2$, $N=10$, $T_a=550$ °C and $t_a=0.5$hr), together with the lattice constants $a$ and $c$ obtained for the non-oriented sample with $x=2$, $y=3.2$, $N=10$, $T_a$=such 350 °C and $t_a=20$ hr. Also shown are the data for the bulk LTP MnBi. The lattice constant $c$ for the c-axis for the oriented thin film increases with temperature almost linearly from 6.061Å at 300K to 6.139Å at 550K. This trend is consistent with the bulk data although the c-axis values are smaller by about 0.7%, compared to the bulk. Also the lattice constant $c$ for the non-oriented sample increases with temperature with a similar slope to that for the oriented one. It is of interest to point out that the $c$-values for the non-oriented sample are very similar to those bulk ones. The present data of the lattice constants will be discussed later in conjunction with magnetic anisotropy.

![Fig.2 The temperature dependence of lattice constant $c$ for the oriented ($T_a=550$ °C and $t_a=0.5$hr) and non-oriented ($T_a=350$ °C and $t_a=20$ hr) LTP MnBi thin films with $x=2$, $y=3.2$, $N=10$, together with the data for bulk10.](image2)

Fig.2 The temperature dependence of lattice constant $c$ for the oriented ($T_a=550$ °C and $t_a=0.5$hr) and non-oriented ($T_a=350$ °C and $t_a=20$ hr) LTP MnBi thin films with $x=2$, $y=3.2$, $N=10$, together with the data for bulk10.

![Fig.3 The magnetization curves for both the field directions along the film normal and film plane at various temperatures for the sample with $x=2$, $y=3.2$, $N=10$, $T_a=550$ °C and $t_a=0.5$hr.](image3)

Fig.3 The magnetization curves for both the field directions along the film normal and film plane at various temperatures for the sample with $x=2$, $y=3.2$, $N=10$, $T_a=550$ °C and $t_a=0.5$hr.
Figure 3 shows the hysteresis curves for fields applied along the film normal and in the film-plane at various temperatures from 50 to 400K for the c-axis oriented film with \(x=2\), \(y=3.2\), \(N=10\), \(T_a=550\) °C and \(t_a=0.5\) hr. It is clearly seen that coercivity drastically increases with increasing temperature, reaching to about 18 kOe at 400K. It is of interest to point out that the M-H curves for both the directions at 50 and 100K exhibits very little coercivity, with the saturation field for magnetization of about 6 kOe, which is roughly equal to the demagnetization field of the thin film at those temperatures. It was reported that the spin reorientation in bulk LTP MnBi takes place at temperatures below about 100K and the magnetization lies in the c-plane at about a temperature below 30K [4],[5]. The present results of the LTP thin film are in qualitative agreement with the earlier bulk data [5].

Fig.4 The temperature dependence of \(K_u\) for the LTP MnBi thin film with \(x=2\), \(y=3.2\), \(N=10\), \(T_a=550\) °C and \(t_a=0.5\)hr. (● Present work and □ Ref.4)

The temperature dependence of the perpendicular magnetic anisotropy constant \(K_u\) estimated by torque measurements is shown in Fig.4, together with the bulk data [4]. It was found that all torques curves measured over the temperature range from 100 to 400K consist largely of the two fold symmetry, indicative of the uniaxial anisotropy mode. The uniaxial magnetic anisotropy constant \(K_u\) of the LTP thin film is found to monotonously increase with temperature from 3x10^6 erg/cc at 150K to 1.5x10^7 erg/cc at 400K, in reasonable agreement with the previous bulk data [4]. The smaller values of \(K_u\) than that for bulk are believed to be due to the fact that a substantial amount (30–40%) of non-magnetic phases such as Bi and Mn are present beside LTP phase, as mentioned above [9]. If one takes into account this fact, then the magnetic anisotropy constant for the present thin film would be nearly the same as that for the bulk value.

Fig.6 Magnetic anisotropy energy of the LTP MnBi calculated within the density functional theory as a function of \(a\) and \(c\) lattice constants. The red line is the lattice constants \(a\) and \(c\), extrapolated to those at 100K and 500K based on the data given in Fig.2 for the present study.

There have been many discussions on the magnetic anisotropy mechanism in conjunction with the saturation magnetization \(M_s\), which is key to understanding the mechanism of a thermally increasing anisotropy [7],[8],[11]-[17]. To our knowledge, there has been discussion in literature relating to the \(M_s\), \(K_u\) correlation for the LTP MnBi bulk/thin films. By identifying the scaling relationship between these two quantities it may be possible to identify the underlying physical mechanism for the increase in effective \(K_u\). In the present case, the saturation magnetization values were estimated from the interpolation of the magnetization curves to the zero-filed values in order to exclude the dia-/paramagnetic contributions. Fig. 5 shows the correlation thus obtained between \(K_u\) and \(M_s\) for a temperature range from 150 to 400K. It is found that the \(K_u\) is inversely proportional to the eighth power of \(M_s\). This is much greater than expected for a first order single and/or two ion model magneto crystalline anisotropy (Ni, Fe (\(n≈3\)) or L1₀FePt (\(n≈2\)) and the sign of the
exponent is opposite (i.e., $K_u$ proportional to $M_s^n$). Such a strong dependence of $K_u$ on $M_s$ in the LTP MnBi thin films is significant for better understanding of the magnetic anisotropy mechanism. This also implies that other contributions to the anisotropy must also be considered. The inserted figure shows the relation between $K_u$ and unit cell volume ($=\sqrt[3]{a^2c}$) for the sample mentioned above. It is of interest to note that the $K_u$ values increase almost linearly with unit cell volume, which is consistent with the theoretical prediction [6].

Calculations were performed with GGA+U theory to account for an effect of coulomb interaction on Mn 3d states. The projected augmented plane wave method was utilized as implemented in VASP package [16]. The effect of spin temperature was taken into account along the lattice temperature using constrained Monte-Carlo method with effective spin Hamiltonian parameterized within the constrained density functional theory to capture magnetic properties scaling. At this stage, the spin temperature effect was taken into account only for single-ion model of magnetic anisotropy with higher order terms (up to $K_3$). Fig. 6 shows the results of first principles and statistical simulations of magnetic anisotropy energy as function of lattice constants ($a$ and $c$). The red line indicates the lattice constants measured and extrapolated to those at 100 and 500K, as shown in Fig.2. It is seen that the change in lattice constant a plays more important role than c, but cannot fully explain the experimental results in LTP MnBi. The spin reorientation experimentally observed at around 100K is not accounted for by the present calculation.

IV. CONCLUSIONS

The temperature dependence of magnetic anisotropy in the LTP MnBi thin films is discussed in conjunction with saturation magnetization and lattice constants. It is experimentally found that $K_u$ is inversely proportional to the 8th power of the saturation magnetization $M_s$. It is also found that the $K_u$ is proportional to the unit cell volume, which is in agreement with the theoretical prediction [7]. The calculation based on first principles of magnetic anisotropy energy as function of lattice constants ($a$ and $c$) and statistical simulations of its spin temperature dependence is consistent with the experimental results. However, the spin reorientation transition taking place at 100K is not accounted for by the present calculation.

ACKNOWLEDGEMENT

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REFERENCES

Magnetic Anisotropy of $\tau$-MnAl Thin Films

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The $\tau$-MnAl alloy exhibits a high magnetic anisotropy energy despite the fact that both Mn and Al elements possess a low spin-orbit coupling constant. In order to understand the magnetic anisotropy mechanism, a systematic experimental study of the correlation between the magnetic anisotropy constant and the saturation magnetization of the $\tau$-phase MnAl thin films has been carried out. A torque measurement has been conducted to determine a uniaxial magnetic anisotropy constant K at various temperatures from 4 to 400 K. It is found that the K is linearly dependent on saturation magnetization $M_s$ over a temperature range from 4 to 400 K. This result is at variance with the theoretical predictions.

Index Terms—magnetic anisotropy mechanism, saturation magnetization, $\tau$-MnAl, torque measurements

I. INTRODUCTION

Manganese alloys with the equiatomic composition such as MnAl, MnGa and MnBi are known for their high magnetic anisotropy constants, attractive for rare-earth free permanent magnet applications [1]. Despite the fact that voluminous work on their magnetic properties and structures has been performed [2, 3], the mechanism of this high magnetic anisotropy energy is not well understood. In the case of MnAl, both Mn and Al elements possess low spin-orbit coupling constants, but the $\tau$-phase MnAl exhibits high magnetic anisotropy constant K in the order of $1 \times 10^7$ erg/cm$^3$ at room temperature [4-6]. Therefore, in order to elucidate the magnetic anisotropy mechanism, a systematic study of the temperature dependence of both the saturation magnetization $M_s$ and magnetic anisotropy constant K in $\tau$-MnAl multilayer thin films has been carried out.

II. EXPERIMENTAL

Multilayer thin films of [Mn (x nm)/Al (y nm)] x N were sputter-deposited onto silica glass substrates at an ambient temperature by using a DC magnetron sputtering system (x, y = 0.5 to 7, N = 10 to 40). The base pressure prior to deposition was below 10$^{-8}$ Torr. The deposition rates for Mn and Al were roughly 0.02 nm/s and 0.03 nm/s, respectively. 5 to 8 nm thick under- and capping-layers of Ru were deposited at ambient temperature before and after the multilayer deposition. The multilayers were post-annealed in high vacuum at various temperatures $T_a$ from 430 ºC to 580 ºC for annealing time $t_a$ up to 600 min. Measurements of magnetic properties were carried out using an alternating gradient magnetometer with applied magnetic fields H up to 1.8 T and a vibrating sample magnetometer in fields up to 9 T over a temperature range 4 K to 400 K. A uniaxial magnetic anisotropy constant K was measured by a torque magnetometer from 4 to 400 K. Structural analyses were performed by a X-ray diffractometer with Co Kα radiation and a transmission electron microscopy.

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetization M at $H = 1.8$ T for samples with $x = 1$, $y = 1.25$, $N = 30$, $T_a = 580$ ºC with various $t_a$ from 10 to 600 min, together with the in-plane coercivity ($H_c//$) and the out-of-plane coercivity ($H_c\perp$). The magnetization M remains nearly constant for $t_a$ from 10 to 130 min, and then decreases with $t_a$ from 190 to 600 min. The decreasing of M could be due to the fact that the $\tau$-phase is not a stable phase at high temperatures, thus tends to decompose into the non-magnetic cubic $\gamma$- and $\beta$-phases. The $H_c\perp$ gradually increases with $t_a$ up to 200 min and then decreases. On the other hand, $H_c//$ remains nearly constant with $t_a$ less than 130 min, but increases with $t_a$ beyond 200 min.

The X-ray diffraction patterns for the same set of the samples are shown in Fig. 2, together with the as-deposited sample. The as-deposited sample shows only the diffraction peaks for f.c.c. Al, h.c.p. Ru under- and overcoat-layers, in addition to some predominant h.c.p. $\epsilon$-MnAl phase. For sample with $t_a = 10$ min, there is a rather sharp peak for $\beta$-Mn, whereas no L1_0 $\tau$-phase peaks are observed. Upon annealing for longer time, the $\tau$-phase
(101) and (110) peaks are observed, though the (110) peaks are rather weaker. As a result, the $H_{c/\parallel}$ increases with increasing $t_a$, as shown in Fig. 1. Furthermore, the peaks for the non-magnetic h.c.p. ε-MnAl phase are observed for all the samples, which may be responsible for the lower magnetization of the thin films than those for bulk. The values of $d_{101}$ of the τ-phase for the samples with $t_a = 190$ and 600 min are 2.143 Å and 2.137 Å, respectively, smaller by 1.8% and 2.1% than the bulk value (= 2.182 Å). There is little change in $d_{101}$ with $t_a$.

The sample with $t_a = 190$ min shows relatively high magnetization and coercivity, and therefore this sample was further examined. Fig. 3 (a) shows the cross-sectional TEM images at different magnifications for the sample with $x = 1, y = 1.25, N = 30, T_a = 580 \degree C$ and $t_a = 190$ min. Little evidence of the multilayer structure is seen in this cross-sectional view. In addition, it can be noticed that the MnAl thin film contains plate-like grains, which may be formed through the martensitic transformation. Fig. 3 (b) shows high resolution cross-sectional image of the same sample. Micro-twins can be observed in the high resolution view, which can be another indication of the martensitic transformation. Fig. 3 (c) shows the fast Fourier transformation image of Fig. 3 (b).

K. The torque curves L were measured from 4 to 400 K in fields from 1 to 9T. The torque curves L were then fitted by Fourier series with $L = A_1 \sin \phi + A_2 \sin^2 \phi + A_3 \sin^3 \phi + A_4 \sin^4 \phi$, where $\phi$ is the angle between the applied field $H$ and the film normal. It was found that except for the torque curves measured at fields below 2 T, all the torque curves can be well fitted to $\sin^2 \phi$ curves, indicating the uniaxial magnetic anisotropy. Therefore, $K$ can be estimated by extrapolating the two-fold symmetry amplitude $A_2$ of the torque curves at different applied magnetic fields to an infinite applied field ($1/H = 0$) and then adding $2\pi M_s^2$ to correct for the demagnetizing effect. Fig. 5 (a) shows the temperature dependence of the $K$ for the sample with $x = 1, y = 1.25, N = 30$ and $T_a = 580 \degree C$, $t_a = 190$ min. It is shown that $K$ decreases with increasing temperature.

According to the previous theoretical calculations [7-9], the normalized magnetic anisotropy constant $K(T)/K(0)$ for 3d metals or alloys was found proportional to $[M(T)/M(0)]^n$, where $n$ is a power law exponent which depends on the magnetic anisotropy mechanism. For example, in the case of a single-ion anisotropy mechanism, $n = 3$, whereas for a two-ion anisotropy mechanism, $n = 2$. The previous results for the L1$_0$ FePt [10] and m-DO$_19$ Fe$_3$Pt [11] alloys were found to be $n = 2$ in reasonable agreement with the theoretical prediction. In order to determine the exponent $n$, the values for $K(T)/K(4K)$ and $M_s(T)/M_s(4K)$ estimated at various measuring temperatures were plotted on a logarithmic scale, each of which is normalized at $T = 4K$. As shown in Fig. 5 (b), the data was fitted to a power relation to acquire the exponent $n$. From the plot, it is found that the value of $n$ is approximately 1. Clearly this result of $n = 1$ is at variance with the theoretical predictions for both the single- and two-ion models. The explanation for $n = 1$ is not found at present. However, according to the recent theoretical work [12], the effective spin-orbit coupling constant in the τ-phase MnAl...
is much larger by almost one order magnitude than those for the individual Mn and Al elements. A more complete theoretical description is required to fully understand the relation between the anisotropy mechanism and the phenomenological power law exponent, n.

IV. SUMMARY

In summary, the present study provides for the first time the correlation between the magnetic anisotropy constant K and the saturation magnetization $M_s$ of the $\tau$-phase MnAl thin films. The results show K and $M_s$ obeys a linear relation law, which is at variance with the theoretical predictions.

ACKNOWLEDGMENT

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REFERENCES


Magnetic and structural properties of Mn-Ga thin films

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Manganese-Gallium system alloys \( \text{Mn}_{3-\delta}\text{Ga} \) are well known for their valuable magnetic properties, including ferromagnetic \( \text{L}_{10} \) structure \( \delta\text{-MnGa} \) [1] and ferrimagnetic \( \text{DO}_{22} \) \( \text{Mn}_{3}\text{Ga} \) [2], both possess high magnetic anisotropy energy in the order of \( 10^7 \text{ erg/cc} \). It has been reported that the \( \text{L}_{10} \) structure \( \text{MnGa} \) can be obtained in the composition range of \( \delta = 1.2-2 \) and the \( \text{DO}_{22} \) type \( \text{Mn}_{3}\text{Ga} \) can be obtained in the composition range of \( \delta = 0.15-1.06 \) [2]. Furthermore, these two phases share the same lattice constant \( a \), indicating the phase transformation between them rather interesting. The present study shows a preliminary study of the magnetic and structural properties of Mn-Ga thin films with various compositions.

Thin films with various compositions were deposited onto silica glass substrates using DC magnetron sputtering. \( \text{MnGa} \) (50-50 at\%) alloy targets and pure Mn targets were used in the deposition process. The precise composition was controlled by changing Mn layer thickness with MnGa layer thickness fixed as 2 nm. The deposited thin films were then post-annealed at a temperature range from 200 to 500 °C. The magnetic properties were characterized by an alternating gradient magnetometer and vibrating sample magnetometer. The structural properties were characterized by X-ray diffraction with Cu K\( \alpha \) radiation and transmission electron microscopy.

As a preliminary result, the \( \text{L}_{10} \) type \( \text{MnGa} \) and the \( \text{DO}_{22} \) type \( \text{Mn}_{3}\text{Ga} \) were successfully fabricated. Fig. 1 and 2 shows the M-H curves and XRD patterns for the deposited Mn-Ga samples. In the case of 2 nm thick Mn layer, a slight peak offset of \( \text{DO}_{22} \) (112) was observed, indicating a lattice distortion of 0.4%. Further study about the phase transformation is on the way.
Fig. 1 M-H curves for Mn-Ga samples with various Mn layer thicknesses.

Fig. 2 XRD patterns for Mn-Ga samples with various Mn layer thicknesses.

Magnetic and structural Properties of MnRh Thin Films fabricated on MgO Substrates

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MnX alloys of about an equiatomic composition such as MnAl, MnBi and MnGa are known to exhibit unique magnetism, in particular possess very high magnetic anisotropy constant K, attractive for permanent magnets and spintorics applications [1]. While bulk MnRh is antiferromagnetic at room temperature, it was reported that the ferromagnetic correlation length increases as Mn concentration increases in the CsCl-type structure [2]. Since then, very little work has been found in literature. Therefore, it is of great interest to study the magnetic properties of MnRh thin films on single crystal substrates and to explore a possibility for high magnetic anisotropy, within the framework of the G8 project, by engineering film-lattice constants thorough film-growth mechanisms.

Multilayer structure \(\{\text{Mn (2.0nm)/Rh (1.0nm)}\} \times 25\), were fabricated onto MgO substrates of (100), (110), and (111) orientations at an ambient temperature in a multi-target UHV confocal sputtering system with the sputtering pressure \(3.9 \times 10^{-3}\) Torr. The samples were subsequently annealed at 500°C for 2 hours in-situ with a vacuum greater than \(10^{-8}\) Torr. Structural analyses were performed by X-ray diffraction (XRD) with Cobalt target. Measurements of magnetic properties were carried out by using a vibrating sample magnetometer over a temperature range from 5 to 400 K in applied fields \(H\) up to 50 kOe.

Figure 1 shows the XRD pattern indicated the CsCl-type structure with lattice constant estimated from (110) peak as \(a_0 = 3.050\) Å for MnRh films grown on MgO substrates of (100), and (110), and \(a_0 = 3.050\) Å for films grown on MgO substrates of (111). The lattice spacing was calculated from equation \([d_{\text{film}} - d_{\text{bulk}}] / d_{\text{bulk}} \times 100\)%). The lattice spacing are in within 0.2% for MnRh films grown on MgO substrates of (100), and (110) and 0.07% for film grown on MgO substrates of (111), with those of bulk MnRh crystal with lattice constant 3.044 Å [3]. The M-H loops show ferromagnetic behavior, unlike bulk, for all the samples with nearly the same \(H_C \sim 750\) Oe for (100), and (110) orientations, and with \(H_C \sim 250\) Oe for (111) orientation (Figure 2.). Figure 3 shows the exchange bias field \((H_{EB})\) for the in plane measurements estimated for MnRh films grown on all the tree substrates and SiO\(_2\). The \(-H_{EB}\) and \(H_C\) increases dramatically below 150K. At 5K the \(H_{EB}\) is calculated to be 210 Oe and 125 Oe for film grown on MgO substrates of (111) while the \(H_{EB}\) for film grown on MgO substrates of (111) orientation was negligible. It is evident that \(H_{EB}\) decreases and disappears around the temperature below 70 K. The \(H_C\) values exhibit a similar trend, indicating a connection between the mechanisms that give rise to coercivity and loop shift.
In summary, the temperature dependent magnetization measurements in MnRh thin films onto MgO single crystal substrates reveals the exchange bias effect accompanied with large coercivity at low temperatures.

References


Figure 1. X-Ray diffraction pattern for MnRh thin films fabricated onto MgO substrates of (100), (110), and (111) orientations. XRD pattern for same films deposited on SiO$_2$ is also included for reference.

Figure 2. M-H loop measured at 5K for in plane measurements.
Figure 3. Temperature dependence of exchange bias field $H_{EB}$. 
Magnetic Properties of LTP MnBi Thin Films Fabricated onto Single Crystal Substrates

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It is well known that the low temperature phase (LTP) of MnBi exhibits unique temperature dependence of coercivity which increases with temperature up to about 500K [1]-[2]. Therefore, LTP MnBi is expected as a candidate for high temperature applications. It is also reported that the magnetic anisotropy is strongly dependent on lattice constant, especially a [3]. In this work, the correlation of magnetic property with the lattice constant of LTP MnBi thin films deposited on single crystal substrates has been investigated.

Multilayers of [Bi(3.2 nm)/Mn(2 nm)]×10 were fabricated onto MgO substrates of (100), (110), and (111) orientations, SrTiO$_3$ substrates of (100) and (110) orientations, and fused silica substrates by using a DC magnetron sputtering system. The multilayered films were deposited at an ambient temperature and subsequently annealed at 450 ºC for 30 minutes in vacuum. After annealing, a capping layer of Ru was deposited at room temperature to prevent oxidation. The crystal structure of the films was characterized by using X-ray diffraction (CuK$_\alpha$) and magnetic properties were measured by using a vibrating sample magnetometer (VSM) in fields up to 18 kOe at room temperature.

It is of interest to note that all the XRD patterns for the samples fabricated onto the various substrates indicate the preferential orientation of the c-axis along the film normal. (Please see Fig.1, which shows the strong (002) peaks of the LTP MnBi at about 29.3 degree.)

The correlation between the magnetic anisotropy, coercivity and lattice constant will be presented.

References:
Fig. 1 The XRD pattern for the MnBi thin films
On the Synthesis of MnBi Nanoparticles

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The objective is to discover a new chemical synthesis of MnBi nanoparticles with a control of the particle size, composition and phase. α-MnBi is ferromagnetic with high value of magnetocrystalline anisotropy energy density (K_u ~ 0.9 x 10⁷ erg/cc). This is a hexagonal phase with the crystallographic c-axis being the magnetic easy axis. These particles would find application in future high data storage density magnetic tape media and in high energy permanent magnets.

The first approach was the simultaneous thermal decomposition of dimanganese decacarbonyl and chemical reduction of bismuth chloride in refluxing phenyl ether in the presence of oleic acid capping ligands. This gave a mixture of ~100 nm diameter Bi particles (Fig. 1) and ~10 nm diameter MnBi particles (Fig. 2). The presence of both Mn and Bi in the particles was confirmed by energy dispersive X-ray analysis (Fig. 3).

This was an exciting result as it demonstrated the MnBi binary alloy particles could be made by a chemical synthesis. The next task was to find a means to avoid the formation of the large Bi particles.

A two stage synthesis avoided the formation of Bi particles. First Mn nuclei were formed by the chemical reduction of manganese chloride in octylether with oleic acid capping ligands. Next bismuth chloride was reduced to bismuth metal in the presence of the Mn nuclei. Reduction conditions were found that gave heterogeneous reduction of Bi³⁺ at the Mn particle surface without homogeneous nucleation and subsequent growth of Bi particles.

Figure 1. Bright field TEM image of the large Bi particles

Figure 2. HAADF image of the small MnBi particles

Figure 3. Energy dispersive X-ray spectrum of the particle circled in red in Fig. 2. The spectrum shows the presence of Bi and Mn in the small particles. The P is present due to the trioctylphosphine ligand.
Optimization of energy product in planar exchange spring permanent magnets using three dimensional micromagnetic simulations

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Abstract:
Exchange spring composites (hard-soft magnetic composites) are interesting for many applications such as rare-earth free permanent magnets [1] and information storage [2]. One key aspect is the figure of merit, the energy product, also called $(BH)_{\text{max}}$. These structures have been proposed to maximize the energy product by making use of the high saturation magnetization of the soft material and the high coercivity of the hard material [3].

Our system of study is a magnetic nano composite where each bilayer consists of a soft and hard magnetic material of total thickness of 22 nm with an easy axis perpendicular to the plane. Using micromagnetic simulations we have investigated the influence of different ratios of the volume of the hard and soft layers on the energy product and the number of bilayer repetitions. Our findings indicate that the maximum energy product depends strongly on the volume ratio as well as on the number of repetitions, as indicated in figure 1. Our simulations also indicate that a higher volume of the soft material can be beneficial for multilayer structures. The optimal volume ratio therefore depends strongly on the repetitions and the strength of the interlayer exchange coupling between the individual layers.

Figure 1: Influence of soft to hard volume ratio and number of repetitions on the energy product. The exchange length in the soft magnetic layer is 2.7 [nm].

In addition we have studied the effect of the exchange length in the soft magnetic material on the energy product. Our calculations show that the exchange length of the soft material affects the reversal process and consequently the value of the energy product. Our findings for different exchange length scales are shown in figure 1 and 2. Our findings indicate that as

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Note: The above text contains mathematical and technical terms that might require specialized knowledge to understand fully.
expected a shorter exchange length results in an optimal structure with a smaller soft to hard magnetic material volume ratio.

![Figure 2](image2.png)

Figure 2: Influence of soft to hard volume ratio and number of repetitions on the energy product. The exchange length in the soft magnetic layer is 1.3 [nm].

In addition we have studied the influence of different anisotropy contributions of the hard and soft magnetic layer on the energy product including a uniaxial or cubic anisotropy for the soft magnet as well as higher order anisotropy contributions in both materials. Our findings indicate that an optimized energy product is relatively insensitive to higher order anisotropy contributions. Figure 3 shows the result of applying uniaxial anisotropy within the soft material.

![Figure 3](image3.png)

Figure 3: Dependence of energy product on uniaxial anisotropy of the soft phase.

Finally we have studied the influence of the interlayer exchange coupling on the energy product, which shows that strong interlayer exchange coupling is necessary to reach a high energy product.

Dynamic instability mechanisms for switching hard grains

Pieter Visscher

We will discuss switching mechanisms and a new method for calculation of switching rates in magnetic systems, with application to switching of grains (domain wall motion) in polycrystalline permanent magnets.

The fundamental theoretical problem in predicting the coercivity of a hard magnet, on a particular time scale, is to calculate the switching rate of a grain (i.e. the probability per unit time that a domain wall will move across it) as a function of applied field. This can be done by formulating and solving a Fokker-Planck equation for the probability distribution, from which the equilibrium distribution and the switching rate can be obtained. For the simplest case of a uniaxial Stoner-Wohlfarth particle, this was done in 1963 by W. F. Brown.

In general, formulating a useful Fokker-Planck equation requires identifying a small set of “slow variables” $s_1, s_2, ...$ such that the system is well described by the probability distribution $\rho(s_1, s_2, ...)$ – the other (“fast”) variables (e.g., short-wavelength spin waves) can be considered to have an equilibrium distribution, for any fixed values of $s_1, s_2, ...$. The uniaxial case is simplest because there is only one “slow variable”, the angle $\theta$ between the magnetization and the easy axis. The azimuthal angle $\phi$ varies rapidly during precession but has no effect on the long-term dynamics. The easy-axis component $m_z$ of the magnetic dipole moment can also be used as the “slow variable”, since $m_z = m_n \cos \theta$.

Of course, in real systems the magnetization is not uniform, as it is in the Stoner-Wohlfarth model. To generalize this approach to non-uniform magnetizations, we have found it useful to use higher moments as additional “slow variables”. For example, in an elongated particle that switches by end nucleation and domain wall motion, the position of the domain wall is determined by the longitudinal moment $m_z = \int M_z d^3r$ and the non-uniformity can be measured by the quadupole moment $q = \int z M_z d^3r$, which vanishes in a uniform system and is maximized by a sharp domain wall. By making a contour plot of the energy in this two-dimensional “slow space”, we can distinguish between different switching mechanisms. The figure shows the energy for a soft-hard composite (center inset) for strong (left figure) and weak (right) exchange.
If exchange were infinitely strong, the particle would switch uniformly with q = 0 (i.e. move along the horizontal $m_z$ axis in the $m_z$–q plane). In the left figure the exchange is strong but not infinite, so the lowest-energy path is bent, but still has its maximum at a saddle point at $q = m_z = 0$. For a larger particle, this point has higher energy than a domain-wall state with the same $m_z$ so the minimum energy path passes $m_z = 0$ in a non-uniform state (nonzero q).

Each point in the “slow space” does not correspond to a single configuration of the system, but to a periodic orbit. Although in the simple Stoner-Wohlfarth case the slow variable $m_z$ is constant along this orbit, unfortunately this is not always true. We have developed a micromagnetic code to calculate these periodic orbits and locate them in the slow space by determining the average values of the moments. In some situations the precession is critical, such as in the case of spin torque switching of a disk. There, we have found that the system begins to switch by uniform precession, but encounters an instability at which the energy can be decreased by moving (in the slow space) in a direction corresponding to formation of a domain wall at the center of the system. This mechanism is not the same as the usual local-nucleation picture, in which nucleation occurs at an edge, not at the center.
We studied the effect of annealing on the integrity of Rh/Mn superlattices [periodic multilayers]. The alloy formation is supposed to yield high energy product magnetic materials. The multilayers have the advantage of easy control of the composition of the total layer. The annealing step following deposition must ensure interdiffusion of the components and formation of the desired phase. Here we use X-ray reflectivity and diffuse scattering to monitor the interdiffusion process. SiO2/{Rh(2.5nm)/Mn(5.0nm)}*10 superlattices were prepared by sputtering. One was measured as deposited and a second sample after heat treatment at 550C for 30 min.

Figure 1. Reflectivity data of as-prepared (black) Mn/Rh superlattice and after annealing (red). The interface roughness amplitude increased from 1.2 nm to 2 nm.
The reflectivity spectra were simulated to extract exact values of layer thicknesses and interface roughness. The layer thicknesses were found to be 3.2 nm Rh and 3.4 nm Mn. The Mn layer roughness was about 1.2 nm and did not change upon annealing while the Rh layer roughness increased from 1 nm to about 2 nm. However, as visible in the reflectivity spectra, the superlattice structure is still well maintained, thus the layers just started to intermix.

Rocking curves taken at the 1st superlattice peak (figure 2) show, besides the sharp central peak, a diffuse scattering intensity close to the center for the as prepared sample [black line] and a much more broadened diffuse intensity for the annealed sample [red line]. This indicates that the interface roughness of the as prepared sample is more chemically sharp but wavy, whereas after annealing interdiffusion has reduced the lateral correlation of the interface roughness.

![Figure 2](image-url)
The diffuse $\theta$-offset scans with $\theta$-offset reveal the level of interface roughness correlation. Clearly, the degree of interface roughness correlation is diminished after annealing as indicated by the diminished intensity of the 1st superlattice Bragg peak, indicating uncorrelated interface roughness typical for interdiffusion.

XRD reflectivity is a useful tool to study the interdiffusion process of multilayers needed to form homogeneous alloys for hard-magnetic applications.

Joseph Green worked on this project within the Computer Based Honors Students program at UA. Afterwards, he did win a scholarship to study a year abroad in Italy and also did win a NOAA Ernest F. Hollings Undergraduate Scholarship.
Magnetic Properties of Co₃O₄ Nanoparticles Fabricated by Chemical Synthesis

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Nanoparticles of cobalt oxide (Co₃O₄), of size 4.2 nm, were fabricated by heating Cobalt (Co) nanoparticles synthesized by using dimethyl sulfoxide (DMSO) solvent. The temperature dependence of magnetization for field cool and zero field cool processes of Co₃O₄ nanoparticles shows the bifurcation at 44 K. A cusp is observed at 1 T and higher applied fields indicating antiferromagnetic behavior in the system with the Néel temperature (Tₕ) ~ 34 K. The estimated magnetic entropy change (-ΔSₘ) for the Co₃O₄ nanoparticles suggests the unusual behavior in magnetic phase transformation of the Co₃O₄ nanoparticles. A normal magnetocaloric effect (MCE) at T ~ 44 K and inverse MCE at T ~ 34 K are observed. These results correlate the magnetocaloric properties to the magnetic phase transitions in the Co₃O₄ nanoparticle system.

Index Terms— Co₃O₄, Nanoparticles, Magnetocaloric effect, Magnetic phase transformation, Dimethyl sulphoxide (DMSO)

I. INTRODUCTION

Magnetic nanoparticles have attracted considerable interest in recent years due to their unique properties, potential for various applications such as permanent magnets where high magnetic anisotropy and high coercivity are essential. Recently, it was reported that nano-particles of Co-carbide synthesized via polyl reactions exhibited very high coercivity, leading to (BH)ₘ₉₅ higher than 20 kJm⁻³ [1, 2]. Bulk spinel ferrites exhibit soft or hard magnetic properties depending on its electronic structure, i.e., bulk CoFe₂O₄ (hard) and MnFe₂O₄ (soft). A recent study involving thin films of (CoFe)₃O₄ reported a magnetic anisotropy of 6x10⁶ erg/cm³ at room temperature [3]. Recently, magnetocaloric effect (MCE) in several spinel oxides has been extensively studied [4-6]. The MCE is an isothermal magnetic entropy (ΔSₘ) or an adiabatic temperature change (ΔTₘ) when the magnetic material is subjected to a varying magnetic field. Magnetic refrigeration based on the MCE is a cooling technology with an environment friendly and energy efficient refrigeration mechanism.

Spinel-type cobalt oxide (Co₃O₄) is a technologically important material due to its diversified applications in many technologies, such as gas sensors, catalytic materials, ceramic materials, and magnetic materials [7-9]. Despite of several techniques to synthesize nanoparticles of spinel Co₃O₄, there has been a great challenge to produce controlled size nanoparticles, as the Co₃O₄ tends to grow into irregular particle-size. Solvent-based synthesis methods can be used to control particle size, but often require the use of surfactant molecules to be attached to the nanoparticle surface in order to reduce oxidation and agglomeration of the particles. It is noted that the presence of the surfactants on the nanoparticle surface has been shown to affect the material’s magnetic properties. Therefore, in order to obtain favorable magnetic properties of the Co₃O₄ nanoparticles, it is essential to maintain the stability of the nanoparticles without negatively affecting the nanoparticle surface by means of added surfactants.

The molecule dimethyl sulfoxide (DMSO) has been reported to successfully serve as both the solvent and the stabilizing agent for the Co nanoparticles during synthesis [6]. The present study is focused on examining the MCE of Co₃O₄ nanoparticles that were synthesized in DMSO and subsequently heat-treated in a controlled manner. The results obtained reveal that the Co₃O₄ nanoparticles show normal and inverse MCE associated with different magnetic phase transition in the system.

II. EXPERIMENTAL METHODS

Cobalt nanoparticles were synthesized via the solvent-based reduction of Co²⁺ using sodium borohydride (NaBH₄) as a reducing agent at room temperature in DMSO solvent. The detailed procedure is described elsewhere [10]. Thermal treatment of the Co nanoparticle powder thus fabricated was performed in air at 1073 K for an annealing time of 16 hours to obtain the Co₃O₄ nanoparticles. Structural analyses were performed using X-ray diffraction (XRD) with Cu-Kα radiation (λ = 0.1540 nm) operated at 40 kV and 40 mA and transmission electron microscopy (TEM). Magnetic measurements were carried out by using a vibrating sample magnetometer capable of measurements over a temperature range from 4 K to 400 K in applied fields H up to 9 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the obtained XRD pattern for Co₃O₄ nanoparticles. It is noted that the Co nanoparticles are transformed from an amorphous structure [10] into spinel Co₃O₄ after annealing. After exposure to 1073 K for 16 hours, the Co nanoparticles become crystalline in structure, as can be observed from sharp peaks in the XRD pattern. The diffraction peaks can be indexed to the spinel structure of Co₃O₄. The TEM image of the Co₃O₄ nanoparticles shows the average particle size (dₐ) to be 4.2 nm (inset of Figure 1).
Figure 2 shows the zero-field cooling (ZFC) and field cooling (FC) magnetization measurements as a function of temperature measured at various \( H \) from 10 mT to 5 T. In each case the sample was cooled down from 300 K to 4 K. A bifurcation of the FC and ZFC magnetization below a temperature \( T \sim 45 \) K is observed, but the bifurcation feature is largely suppressed at \( H=1 \) T. A bifurcation in the ZFC and FC curves generally shows the co-existing ferromagnetic (FM) and antiferromagnetic (AFM) phases in the system. It is noted that both the ZFC and FC magnetization curves also show a cusp at \( T=34 \) K at \( H=1 \) T. Above \( H=1 \) T, it is believed that most of the ferromagnetic domains are aligned to the direction of the applied magnetic field. The position of the cusp peak is found to be independent of the applied magnetic field. This result implies that the cusp is related to the AFM to paramagnetic (PM) transition. In addition to the AFM-PM transition the cusp appears to be associated with the contribution from a ferromagnetic phase having a curie temperature \( (T_C) \) about 45 K.

\[ \Delta S_M = \mu_0 \frac{\partial M}{\partial H} dH, \]

where \( M \) is the magnetization, \( H \) is the magnetic field, \( \mu_0 \) is the permeability, and \( T \) is the temperature [12]. The peaks near the magnetic transition are found in the temperature dependent of entropy resulted from integration between the \( M \) Vs \( H \) curves. Isothermal magnetizations curves were measured for applied field (\( H \)) up to 5 T with the field steps of 0.1 T. The value of \( \Delta S_M \) was calculated by numeric integration of above equation over the field span of 5 T. The temperature difference \( \Delta T \) between two successive isotherms was used. Fig. 5 shows the magnetic entropy change \( -\Delta S_M \) as a function of temperature for different magnetic field changes up to 5 T for \( Co_3O_4 \) nanoparticles. The \( -\Delta S_M \) for \( Co_3O_4 \) nanoparticles shows the unusual behavior with the normal MCE at \( T \sim 44 \) K that reaches a value of 0.78 J/kg K for \( \Delta H=5 \) T, and inverse MCE at \( T \sim 34 \) K with a value of 0.85 J/kg K for \( \Delta H=5 \) T. The temperature \( (34 \) K) which corresponds to the inverse MCE peaks is related to the magnetic transition between the AFM and the FM phase. These trends in MCE correspond to antiferromagnetic ordering below 34 K, and a weak ferromagnetic phase aligned in paramagnetic state above 34 K. The observed temperature dependence of the MCE may be explained if both the phases with different, but close, transition temperatures \( (T_N \geq T_N) \) coexist in the \( Co_3O_4 \) nanoparticle sample: the MCE is positive \( (\Delta S_M>0) \) and negative \( (\Delta S_M<0) \) near the FM transition \( (T_C=44 \) K) and AFM transition \( (T_N=34 \) K), respectively.

It should be noted that the inverse MCE was observed at and above the \( \Delta H=0.5 \) T, which is also seen from the \( M-T \) data in (Fig 2) as the field is needed to freeze the antiferromagnetic phase. The position of the inverse MCE peak is independent of the applied magnetic field that is in agreement with the cusp in the magnetization data that is independent of the applied field. This distinctive feature is attributed to the coexisting AFM-FM phases and the interplay between these phases is determined by the applied magnetic field [13].

In order to elucidate the influences of the magnetic transition on MCE in \( Co_3O_4 \) nanoparticles, the magnetic entropy change was calculated from a series of \( M(H) \) isotherms through the application of the thermodynamic Maxwell relation.

\[ \Delta S_M = \mu_0 \frac{\partial M}{\partial H} dH, \]

where \( M \) is the magnetization, \( H \) is the magnetic field, \( \mu_0 \) is the permeability, and \( T \) is the temperature [12]. The peaks near the magnetic transition are found in the temperature dependent of entropy resulted from integration between the \( M \) Vs \( H \) curves. Isothermal magnetizations curves were measured for applied field (\( H \)) up to 5 T with the field steps of 0.1 T. The value of \( \Delta S_M \) was calculated by numeric integration of above equation over the field span of 5 T. The temperature difference \( \Delta T \) between two successive isotherms was used. Fig. 5 shows the magnetic entropy change \( -\Delta S_M \) as a function of temperature for different magnetic field changes up to 5 T for \( Co_3O_4 \) nanoparticles. The \( -\Delta S_M \) for \( Co_3O_4 \) nanoparticles shows the unusual behavior with the normal MCE at \( T \sim 44 \) K that reaches a value of 0.78 J/kg K for \( \Delta H=5 \) T, and inverse MCE at \( T \sim 34 \) K with a value of 0.85 J/kg K for \( \Delta H=5 \) T. The temperature \( (34 \) K) which corresponds to the inverse MCE peaks is related to the magnetic transition between the AFM and the FM phase. These trends in MCE correspond to antiferromagnetic ordering below 34 K, and a weak ferromagnetic phase aligned in paramagnetic state above 34 K. The observed temperature dependence of the MCE may be explained if both the phases with different, but close, transition temperatures \( (T_N \geq T_N) \) coexist in the \( Co_3O_4 \) nanoparticle sample: the MCE is positive \( (\Delta S_M>0) \) and negative \( (\Delta S_M<0) \) near the FM transition \( (T_C=44 \) K) and AFM transition \( (T_N=34 \) K), respectively.

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V. ACKNOWLEDGEMENT

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FIG. 3. M-H isotherms curves for Co$_3$O$_4$ nanoparticles measured from 36 K to 100 K. The inset shows the $M-H$ isotherms measured from 4 K to 34 K.

FIG. 4. Arrott plots for Co$_3$O$_4$ nanoparticles near the magnetic transition temperature (a) from 26 K to 34 K and (b) from 36 K to 46 K.

FIG. 5. Temperature dependence of $-\Delta S_M$ at different applied fields up to 5 T for Co$_3$O$_4$ nanoparticles. The inset shows the $-\Delta S_M$ around 34 K for $\Delta H$ from 0.5 T to 1 T.