Influence of Negative Field Cooling on the Exchange Bias Properties of Potassium Split Graphene Nanoribbons

M. Venkat Narayana¹, Srinivasa Rao Singamaneni² and Suryanarayana Jammalamadaka^{1*}

1. Magnetic Materials and Device Physics Laboratory, Department of Physics, IIT Hyderabad, Telangana 502285, India

2. Department of Physics, University of Texas at El Paso, El Paso, Texas 79968, USA

Abstract: We demonstrate the evidenced exchange bias properties of graphene nanoribbons (GNRs) with the negative magnetic field cooling. Upon the negative field cooling from 300 K to 5 K, the hysteresis loop shifts along the negative magnetic field axis, that coincides with the cooling field direction. This observation indicates that there exists a positive exchange bias in GNRs. Furthermore, enhanced exchange bias was observed when the polarity of field cooling is negative as compared with positive field cooling, hinting that there might be complex interplay between orbital and spin degrees of freedom. In addition, the variation of exchange bias and the coercive field as a function of negative cooling field is also studied.

Key words: Exchange bias, coercive field, field cooling, graphene nanoribbons, hysteresis loop.

1. Introduction

Utilization of the spin degree of freedom in addition to the orbital one in the magnetic nanostructures has given an opportunity in exploring them in the data storage devices [1]. Novel properties can be realized from the aforesaid devices since the length scales of them would alter [2]. Among the most appealed properties in recent past, exchange bias (EB) phenomena has gained much interest due to the fact that it can be utilized in various data storage devices such as the magnetic random access memory and the spin valve structures [3-8]. Essentially, EB effect is an interface phenomenon, which can be induced in the systems consisting of ferromagnetic (FM) – antiferromagnetic (AFM) [3], FM – spin glass (SG) [9], AFM – ferrimagnetic (FI) [10, 11] and FM – FI [12] interfaces. Exchange bias or exchange anisotropy can be realized as a shift in the hysteresis loop along the magnetic field axis up on cooling the FM – AFM

interface through a Néel temperature (T_N) of AFM in the presence of the magnetic field [3]. It has been believed that the pinned spins at the interface results in shift of the hysteresis loop along magnetic field axis. In general, if the loop shifts opposite to the cooling field direction it is called as the negative EB and if loop shifts along the cooling field direction it is called as the positive EB [7].

Due to the high carrier mobility, long spin life time resulting from the low spin-orbit coupling ($\sim 10^{-4}$ eV) and the low hyperfine interaction of graphene at room temperature, it has been believed that it is promising material for the spintronic applications [13, 14]. On the other hand, the graphene nanoribbons (GNRs) are thin layers of the graphene which are characterized by the magnetic zigzag edges and apparently are absent in the graphene [15-17]. Existence of the long range magnetic ordering among the edge states of GNRs has been demonstrated by the first principle calculations [15, 18]. It has been believed that the long range magnetic ordering is a FM if there is a coupling between the spins that residing on the same edges,

*Corresponding author: Suryanarayana Jammalamadaka, assistant professor, research fields: magnetic materials and devices, 2D materials and mesoscopic materials.

however, this would be an antiferromagnetic (AFM) if the coupling occurs between the opposite edges. Such magnetic, EB and the dynamic response of EB of potassium splitting of the multiwalled carbon nanotubes (GNRs) have been paralleled by experimental observations recently [19]. Possible sources for the observed ferromagnetism has been suggested from the clustering of magnetic fragments comprises of carbon defects coupled with hydrogen. On the other hand, observed negative exchange bias in the GNRs up on a positive cooling field has been attributed to the presence of the AFM regions mixed with a FM phase [20]. A plethora of experimental investigations have proved that negative magnetic field cooling (NFC) would have pronounced effects on exchange bias properties [21-23]. Such marked results pertinent to exchange bias have been attributed to existence of pinned and rotatable spins at the interfaces. Hence, in the present manuscript, we demonstrate the effect of negative magnetic field cooling on exchange bias properties of GNRs.

2. Experimental

The GNRs were produced directly from the unzipping of the carbon nanotubes as reported by Tour's group [24]. In this process, the potassium metal and the multiwall carbon nanotubes were sealed in a glass tube and heated at 250 °C for about 14 h in the furnace and subsequently quenched to affect the longitudinal splitting process. Further this splitting process assisted by the generation of the H₂ upon the ethanolic quench. Finally, the GNRs which are free from the oxidative damage, are obtained from the exfoliation of the multiwall carbon nanotubes upon the sonication in a chlorosulfonic acid. Structural and microstructural measurements have been reported on GNRs [24]. The magnetization measurements were carried out using a physical property measurement system which consists of a vibrating sample magnetometer (Quantum design) in the temperature range of 5-300 K and up to the maximum magnetic

field of 10 kOe. The samples were cooled in the presence of the negative magnetic field to a desired temperature, 5 K and then the hysteresis loops were recorded.

3. Results and Discussion

Now, we discuss the results of the magnetization in exploring the EB effect in the GNRs. In our earlier work [19], we have reported that the low temperature susceptibility of the GNRs exhibits a peak at 70 K under the zero field conditions (ZFC), such a broad maximum has been correlated to the competing interaction between various FM and AFM magnetic phases. Such competing interactions lead to a negative EB upon positive field cooling. In the present work, the GNRs were cooled under ZFC and NFC conditions from 300 K. During ZFC process, no magnetic field was applied. However, under NFC condition, GNRs were cooled from 300 K to 5 K in the presence of the negative magnetic fields: -1, -2, -3 and -4 kOe and the corresponding hysteresis loops were recorded between -10 kOe and 10 kOe.

From Fig. 1, it is clear that for GNRs, there exists hysteresis with coercivity (~200 Oe) at 5 K. It is also evident that magnetization is not saturated as though we need to apply higher fields to saturate. In order to validate the observed magnetization graphs, curves are fitted with the Langevin function. Fig. 2 depicts the fitted isothermal magnetization graph at 5 K with the Langevin function which is valid for the classical spins of $S = 1/2$, which describes the disordered magnetic behavior. The equation that we used is given as:

$$M = M_0 \left[\text{Coth}\left(\frac{m_0 m_B H}{k_B T}\right) - \left(\frac{m_0 m_B H}{k_B T}\right)^{-1} \right] \quad (1)$$

where, M is the magnetization, μ_0 is the permittivity of vacuum, $\mu_B = 9.274 \times 10^{-24}$ J/T is the Bhor magneton, $k_B = 1.381 \times 10^{-23}$ J/T is the Boltzmann constant, M_0 is the saturation magnetization in emu/g, $T = 5$ K. From the fitting, large value of the theoretical magnetic moment is observed, which suggests the clustering of

Fig. 1 Isothermal M-H loops at 5K under ZFC and NFC conditions. Bottom inset (a) shows the expanded view of shift in the hysteresis loop along negative field axis, which demonstrates the positive exchange bias.

Fig. 2 Langevin function fit for the magnetization curve at 5 K.

the $S = \frac{1}{2}$ spins. The possibility of the cluster magnetism in the graphene-derived materials has been observed earlier in literature by various groups [25-27]. Furthermore, there exists a loop opening at the origin which indicates ferromagnetic behavior. It is also apparent that the hysteresis loop is symmetric with respect to the magnetic field axis, under the ZFC conditions. However, in NFC condition, hysteresis loop shifts along the negative magnetic field axis, which may be due to the pinning of the spins at FM

and AFM interface. Essentially, the hysteresis loop shifts along the negative field axis as shown in inset of Fig. 1, which indicates a positive exchange bias due to the pinned spins at the interface which are coupled antiferromagnetically. Similar variation of exchange bias has been observed in epitaxial $\text{BiFeO}_3\text{-La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ heterostructures [21]. Observed positive exchange bias can be explained on the basis of the competing exchange interaction between the FM - AFM phases and the coupling between an applied magnetic field – and spins which are aligned antiferromagnetically at the surface [4]. Essentially, there exists a complex interplay between various phases and externally applied magnetic field. In general if the interfacial interaction at FM/AFM interface is FM or AFM, negative exchange bias would be evident. In contrast, in order to realize a positive exchange bias, the interfacial interaction must be AFM. Hence, we believe that in GNRs up on NFC, AFM coupling exists between the two magnetic phase.

Such a strong AFM interaction leads to a large interface magnetic energy which may demand large cooling field (H_{FC}) to align the antiferromagnetic surface magnetization along the cooling field (H_{FC}). However, it is very interesting to note in our present investigation that with few kOe of H_{NFC} , it is possible to observe positive EB in GNRs despite having an anticipated AFM interface between the FM and the AFM phases. Earlier positive EB has been observed in FeSn-FeGd ferromagnetic and ferrimagnetic bilayers by Canet *et al.*, and such effect has been attributed to the located domain wall at the interface [28]. Keet. *et al.*, have reported a positive EB in the ferromagnetic $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) / SrRuO_3 (SRO) bilayers due to an AFM interfacial coupling between the ferromagnetic LSMO and SRO layers [29]. Harkirat Singh *et al.* reported the phenomenon of positive EB in all ferromagnetic layered soft/hard Fe/Co spring magnetic system, in this system they argued the reason for observed positive EB is due to the AFM

exchange coupling at the interface as a result of intermixing of Fe into the Co layer [30]. Both the positive and negative EB effects have been observed in the perovskite manganite in NdMnO_3 as Nd^{3+} ordering is induced by Mn^{3+} FM component and consequently couple antiferromagnetically to each other, which leads the exchange bias effect. Such positive EB has been observed at 10 T [31]. The noteworthy observation in the present GNRs is that we could see a positive EB with few kOe magnetic fields under the NFC conditions.

Now we quantify the aforesaid positive EB (H_E) and coercivity (H_C) values from the loop opening using the equations:

$$H_{EB} = \frac{(H_{CL} + H_{CR})}{2} \quad (2)$$

$$H_C = \frac{(H_{CR} - H_{CL})}{2} \quad (3)$$

where, H_{CL} and H_{CR} are left and right coercive fields of the hysteresis loop. Variation of the H_E and the H_C with respect to the negative cooling field strength H_{NFC} is depicted in the Figs. 3a and 3b respectively. From Fig. 3a, it is apparent that the H_E increases up to a critical field (1 kOe) and diminishes above the critical field. Such a variation of H_E exactly mimics the variation of EB in phase separated perovskite manganites. The variation of the H_E vs. H_{NFC} could be fitted with the following equation [32]:

$$-H_E \propto J_i \left[\frac{J_i \mu_0}{(g \mu_B)^2} L \left(\frac{\mu H_{NFC}}{k_B T_f} \right) + H_{NFC} \right] \quad (4)$$

where, $L(x)$ is the Langevin function, where $x = \mu H_{NFC} / k_B T_f$, $\mu_B = 9.274 \times 10^{-24}$ J/T is the Bohr magneton, $k_B = 1.381 \times 10^{-23}$ J/K is the Boltzmann constant and μ is the magnetic moment of the clusters, g is the gyromagnetic factor, J_i is the interface exchange coupling constant, H_{NFC} is the cooling field, and $T_f = 5$ K. Extracted negative value of the J_i ($J_i < 0$) from fitting indicates that there exists an AFM coupling between the FM and AFM phases, which is in consistent with our earlier discussion. From the

exchange bias variation, a maximum value of $H_E \sim 52$ Oe is observed when the GNRs were cooled with negative field of 1 kOe. On the other hand, previously, a maximum H_E of 40 Oe has been observed upon cooling the GNRs with a positive field value of 4 kOe [19]. Our results are in accordance with the work done by Wu *et. al* [22], where they reported exchange bias properties of BFO/LSMO heterostructure. The magnitude of H_E is higher when BFO is negatively polarized and lower when BFO is positively polarized by an applied electric field. Such intriguing phenomenon has been attributed to the presence of both the pinned and rotatable spins at the interface. We strongly believe that similar phenomena might be

Fig. 3 Demonstrates the variation of (a) exchange bias (H_E) and (b) coercivity (H_C) with respect to the negative cooling field (H_{NFC}). It is evident from the graph that variation of EB and coercivity is similar up to 1 kOe. However, above that EB decreases and coercivity is sluggish as though it would saturate.

happening in GNRs as well. This certainly requires additional measurements, which is of our future goal. Fig. 3b demonstrates the variation of the H_C with respect to the H_{NFC} . The variation of H_C exactly mimics the variation of H_E until the critical field which is in striking coincidence. Such intriguing variation of the H_E can be explained on the basis of the fact that the pinning of the magnetic moments at the FM - AFM interface of the GNRs which sets in when the GNRs are cooled down to 5 K in the presence of the magnetic fields and leads to a large increase in the H_E . At higher H_{NFC} , the effective magnetic coupling (Zeeman coupling) between the field and the AFM moments increases, which further orients the AFM moments along the field direction. At that stage, the Zeeman coupling over comes the exchange coupling at the interface of the FM-AFM, leading to a decrease in EB field [20]. On the other hand, H_C increases initially and sluggish at higher fields, which is typical for an EB system. Similar variation for H_C has been observed in EB systems by other groups [33-35]. However, a complete understanding of positive EB in potassium split GNRs upon negative field cooling which is being planned.

4. Conclusions

With the negative field cooling a positive exchange bias prevailed in GNRs and such intriguing phenomenon is attributed to existence of strong antiferromagnetic coupling between competing FM and AFM phases. Enhanced exchange bias value was observed up on negative field cooling. It is believed to be due to existence of pinned and rotatable spins at the interfaces. Obtained results from fitting of the variation of exchange bias field with cooling field indicates a negative exchange coupling coefficient, which is in consistent with the observed positive exchange bias. These experimental findings will be helpful in developing graphene based spintronic devices.

Acknowledgements

We would like to thank Indian Institute of Technology Hyderabad for the financial support.

References

- [1] Parkin, Stuart S. P., Kaiser, C., Panchula, A., Rice, P. M., Hughes, B. and Samant, M. 2004. "Giant Tunnelling Magnetoresistance at Room Temperature with MgO (100) Tunnel Barriers." *Nature Materials* 3: 862-7.
- [2] Han, W., Kawakami, R. K., Gmitra, M. and Fabian, J. 2014. "Graphene Spintronics." *Nature Nanotechnology* 9: 794807.
- [3] Meiklejohn, W. H. and Bean, C. P. 1957. "New Magnetic Anisotropy." *Phys. Rev* 105: 904-13.
- [4] Nogués, J., Lederman, D., Moran, T. J. and Schuller, I. K. 1996. "Positive Exchange Bias in FeF₂-Fe Bilayers." *Phys. Rev. Lett* 76: 4624-7.
- [5] Scholl, A., Liberati, M., Arenholz, E., Ohldag, H. and Stöhr, J. 2004. "Creation of an Antiferromagnetic Exchange Spring." *Phys. Rev. Lett* 92: 247201.
- [6] Wu, J., Park, J. S., Kim, W., Arenholz, E., Liberati, M. and Scholl, A. *et al.* 2010. "Direct Measurement of Rotatable and Frozen CoO Spins in Exchange Bias System of CoO/Fe/Ag(001)." *Phys. Rev. Lett* 104: 217204.
- [7] Nogués, J. and Schuller, I. K. 1999. "Exchange Bias." *Journal of Magnetism and Magnetic Materials* 192: 203-32.
- [8] Jammalamadaka, S. N., Vanacken, J. and Moshchalkov, V. V. 2012. "Exchange Bias and Training Effects in Antiferromagnetically Coupled La_{0.7}Sr_{0.3}MnO₃/SrRuO₃ Superlattices." *Europhysics Letters* 98 (5): 17002-6.
- [9] Ali, M., Adie, P., Marrows, C. H., Greig, D., Hickey, B. J. and Stamps, R. L. 2007. "Exchange Bias Using a Spin Glass." *Nature Materials* 6: 70-5.
- [10] Mangin, S., Marchal, G. and Barbara, B. 1999. "Evidence of Exchange-Bias-Like Phenomenon in GdFe/TbFe/GdFe Domain Wall Junctions." *Phys. Rev. Lett* 82: 4336-9.
- [11] Zaag, P. J. van der, Wolf, R. M., Ball, A. R., Bordel, C., Feiner, L. F. and Jungblut R. 1995. "A Study of the Magnitude of Exchange Biasing in [111] Fe₃O₄/CoO Bilayers." *Journal of Magnetism and Magnetic Materials* 148: 346-8.
- [12] Cain, W. C. and Kryder, M.H. 1990. "Investigation of the Exchange Mechanism in NiFeTbCo Bilayers." *J. Appl. Phys* 67: 5722-4.
- [13] Soriano, D., Munoz-Rojas, F., Fernandez-Rossier, J. and Palacios, J. J. 2010. "Hydrogenated Graphene Nanoribbons for Spintronics." *Phys. Rev. B* 81: 165409.
- [14] Yazyev, Oleg V. 2008. "Magnetism in Disordered

- Graphene and Irradiated Graphite.” *Phys. Rev. Lett* 101: 037203.
- [15] Son, Y.-W., Cohen, M. L. and Louie, S. G. 2006. “Energy Gaps in Graphene Nanoribbons.” *Phys. Rev. Lett* 97: 216803.
- [16] Yang, L., Park, C.-H., Son, Y.-W., Cohen, M. L. and Louie, S. G. 2007. “Quasiparticle Energies and Band Gaps in Graphene Nanoribbons.” *Phys. Rev. Lett* 99: 186801.
- [17] Fujita, M., Wakabayashi, K., Nakada, K. and Kusakabe, K. 1996. “Peculiar Localized State at Zigzag Graphite Edge.” *J. Phys. Soc. Jpn* 65: 1920-3.
- [18] Pisani, L., Chan, J. A., Montanari, B. and Harrison, N. M. 2007. “Electronic Structure and Magnetic Properties of Graphitic Ribbons.” *Phys. Rev. B* 75: 064418.
- [19] Rao, S. S., Jammalamadaka, S. N., Stesmans, A., Moshchalkov, V. V., Tol, J. van and Kosynkin, D. V. *et al.* 2012. “Ferromagnetism in Graphene Nanoribbons: Split versus Oxidative Unzipped Ribbons.” *Nano Lett* 12: 1210-7.
- [20] Jammalamadaka, S. N., Rao, S. S., Vanacken, J., Moshchalkov, V. V., Lu, W. and Tour, J. M. 2012. “Dynamic Response of Exchange Bias in Graphene Nanoribbons.” *Appl. Phys. Lett* 101: 142402.
- [21] Rao, S. S., Prater, J. T., Wu, F., Shelton, C. T., Maria, J.-P. and Narayan, J. 2013. “Interface Magnetism in Epitaxial $\text{BiFeO}_3\text{-La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Heterostructures Integrated on Si (100).” *Nano Letters* 13: 5814-21.
- [22] Wu, S. M., Cybart, S. A., Yu, P., Rossell, M. D., Zhang, J. X. and Ramesh, R. *et al.* 2010. “Reversible Electric Control of Exchange Bias in a Multiferroic Field-Effect Device.” *Nature Materials* 9: 756-61.
- [23] Wu, S. M., Cybart, S. A., Yi, D., Parker, J. M., Ramesh, R. and Dynes, R. C. 2013. “Full Electric Control of Exchange Bias.” *Phys. Rev. Lett* 110: 067202.
- [24] Kosynkin, D. V., Lu, W., Sinitskii, A., Pera, G., Sun, Z.-Z. and Tour, J. M. 2011. “Highly Conductive Graphene Nanoribbons by Longitudinal Splitting of Carbon Nanotubes Using Potassium Vapor.” *ACS Nano* 5: 968-74.
- [25] Boukhvalov, D. W. and Katsnelson, M. I. 2011. “Sp-Electron Magnetic Clusters with a Large Spin in Graphene.” *ACS Nano* 5: 2440-6.
- [26] Rode, A. V., Gamaly, E. G., Christy, A. G., Fitz Gerald, J. G., Hyde, S. T. and Elliman, R. G. *et al.* 2004. “Unconventional Magnetism in All-Carbon Nanofoam.” *Phys. Rev. B* 70: 054407.
- [27] Gerber, I. C., Krashenninnikov, A. V., Foster, A. S. and Nieminen, R. M. 2010. “A First-Principles Study on Magnetic Coupling between Carbon Adatoms on Graphene.” *New Journal of Physics* 12: 113021.
- [28] Canet, F., Mangin, S., Bellouard, C. and Piecuch, M. 2000. “Positive Exchange Bias in Ferromagnetic-Ferrimagnetic Bilayers: FeSn/FeGd .” *Europhys. Lett* 52: 594-600.
- [29] Ke, X., Rzechowski, M. S., Belenky, L. J. and Eom, C. B. 2004. “Positive Exchange-Bias in Ferromagnetic $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ / SrRuO_3 Bilayers.” *Appl. Phys. Lett* 84: 5458.
- [30] Harkirat, S., Gupta, R., Chakraborty, T., Gupta, A. and Mitra, C. 2014. “Study of Exchange Bias in All Ferromagnetic Fe/Co Soft/Hard Bilayer.” *IEEE Transactions on Magnetics* 50: 1-4.
- [31] Hong, F., Cheng, Z.-X., Wang, J.-L., Wang, X.-L. and Dou, S.-X. 2012. “Positive and Negative Exchange Bias Effects in the Simple Perovskite Manganite NdMnO_3 ,” *Appl. Phys. Lett* 101: 102411.
- [32] Niebieskikwiat, D. and Salamon, M. B. 2005. “Intrinsic Interface Exchange Coupling of Ferromagnetic Nanodomains in a Charge Ordered Manganite.” *Phys. Rev. B* 72: 174422-9.
- [33] Karmakar, S., Taran, S., Bose, E., Chaudhuri, B. K., Sun, C. P. and Huang, C. L. *et al.* 2008. “Evidence of Intrinsic Exchange Bias and its Origin in Spin-Glass-Like Disordered $\text{L}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ Manganites ($\text{L} = \text{Y}, \text{Y}_{0.5}\text{Sm}_{0.5}$, and $\text{Y}_{0.5}\text{La}_{0.5}$.)” *Phys. Rev. B* 77: 144409.
- [34] Giri, S. K., Poddar, A. and Nath, T. K. 2011. “Surface Spin Glass and Exchange Bias Effect in $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ Manganites Nanoparticles.” *AIP Advances* 1: 032110.
- [35] Jammalamadaka, S. N., Rao, S. S., Bhat, S. V., Vanacken, J. and Moshchalkov, V. V. 2012. “Oscillatory Exchange Bias and Training Effects in Nanocrystalline $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.” *AIP Advances* 2: 012169.