Magnetism and Magnetoelectric Effect in Thin Films and Bilayers of Chromia

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RENU

(E. NO. D12084)

School of Basic Sciences

Indian Institute of Technology Mandi

Mandi-175001, India

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ABSTRACT

Thin film and multilayer studies have opened up many advanced areas of research in material science which have potential applications in electronics, semiconductor devices, transistors, integrated circuits, memory devices, data storage, spintronics, optoelectronics etc. Many experimental and theoretical studies have been done to understand the electronic, structural, and magnetic properties of the thin films [1-3]. Experimental investigations are not only labor intensive, difficult to perform, expensive but also time-consuming especially, when the geometry is not well understood. A theoretical/computational investigation is helpful in this regard. First principle or *ab-initio* calculations based on density functional theory (DFT), and analytical model are the two important tools to understand a material at the atomic level with a very low cost. These theoretical/computational approaches are useful in the prediction of a new possible combination of the materials as well as to understand the previous experimental results. Bulk Cr_2O_3 is a room temperature magnetoelectric (ME) material. But the magnetoelectric effect in thin films of Cr_2O_3 is less studied, making the chromia thin film an interesting material to explore. Moreover, a contradiction in experimental reports and lack of theoretical studies on the magnetism in Cr_2O_3 thin films encouraged us to study the Cr_2O_3 thin film using first principle calculations. The first principle and analytical studies of magnetic and magnetoelectric properties of a chromia (Cr_2O_3) thin film, spin polarization in the bilayers of the Cr_2O_3 with graphene (Gr) and interface exchange interaction in cobalt-chromia (Co-Cr_2O_3) bilayer are included in the present. To start with, we have introduced the magnetic and magnetoelectric properties of thin films and multilayers briefly and concisely. Therefore, introduction about the magnetic and magnetoelectric properties of thin films and multilayers has been given. We have also discussed the theory of methods, used in the calculations to study the films and bilayers. Because of lack of theoretical understanding of Cr_2O_3 thin films, the magnetism of Cr_2O_3 free-standing thin films as well as on α-Al_2O_3 are explored by considering three Cr_2O_3 films having thicknesses of 4.1 Å (I), 6.7 Å (II), and 10.9 Å (III) and comparing the spin structures of free films with those on the substrate. For the free films, we find that film I is ferromagnetic (FM), while II and III are antiferromagnetic (AFM). On the substrate,

the Cr_2O_3 film I is also FM. Films II and III remain basically AFM, although the spins of the top Cr layers change sign in both films, create a ferrimagnet with a small uncompensated net moment.

In addition, the effect of Cr_2O_3 (0001) thin film on spin polarization of a graphene layer is also explored. The magnetic moment in graphene is a proximity effect and can be regarded as a second-order Stoner scenario, and similar mechanisms are likely realized for all-graphene systems with an insulating magnetic substrate. In the absence of charge transfer, the magnetic moment would be quadratic in the exchange field, as contrasted to the usually encountered approximately linear dependence. The net magnetization of the graphene is small, of the order of 0.01 μ_B per atom, but the energy-dependent spin polarization exhibits pronounced peaks that have a disproportionally strong effect on the spin-polarized electron transport and are therefore important for spin electronics applications.

We have also investigated how an external electric field affects the magnetic moment in the Cr_2O_3 thin film and controls the spin polarization in graphene on Cr_2O_3, a system of interest in the area of spin field-effect transistors. Both free-standing Cr_2O_3 thin films and graphene-bilayers are considered. The effect of the electric field depends on the thickness of the Cr_2O_3 and ranges from moderately strong and linear effects to very strong nonlinear magnetoelectricity. The graphene modifies and generally enhances the nonlinear magnetoelectric effect. We also find that the external electric field drastically changes the energy-dependent spin polarization in the graphene layers, which is predicted to reach values of up to about 80%.

Bilayers of ferromagnetic (FM) and antiferromagnetic (AFM) materials are known as exchange bias systems in spin electronics. Additional functionality of these exchange biased systems can be achieved by applying an external electric field if AFM film of FM/AFM system shows magnetoelectric behavior also. Such systems have been proposed as crucial components for memory devices. A better understanding of the exchange interactions at the interface of FM cobalt film and AFM+ME Cr_2O_3 film would contribute in spintronics. Therefore, interface exchange interactions in the Co-on-Cr_2O_3 (0001) system are also investigated in this work. Density-functional theory predicts the exchange coupling at the interface to be antiferromagnetic, in agreement with earlier experimental results. The spin-polarized photoemission spectra reveal both perpendicular and in-plane magnetization components, in the cobalt adlayer on Cr_2O_3. A magnetization canted with respect to the surface normal, inferred from the presence of remnant spin polarization both in the plane of the cobalt film and along the surface normal may be understood as a micromagnetic canting effect involving magnetostatic self-interaction and exchange coupling between Co and Cr_2O_3.

Further, to understand the interface interaction of Co/Cr_2O_3 bilayer, this work also includes the study of interface exchange coupling as a function of the electric field for the bilayer Co/Cr_2O_3 and trilayer Co/Pt/Cr_2O_3. The sign and magnitude of the interface exchange depend on the thickness of the cobalt layer, and oscillatory sign changes of the interface exchange are found in the trilayer system. The electric-field dependence of the exchange, especially the sign changes in Co/Pt/Cr_2O_3, may be exploited in voltage controlled spin-electronics applications.

The aim of the present work is to give a better insight of the magnetic behavior of the Cr_2O_3 thin films and layered structure of Cr_2O_3 with Gr and Co by applying the electric field. Drastic changes in a magnetic moment, spin polarization and exchange interactions of the Cr_2O_3, Gr/Cr_2O_3, Co/Cr_2O_3 and Co/Pt/Cr_2O_3 films in the presence of the electric field make the systems potential candidates for spintronics devices.

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Renu
School of Basic Sciences
Indian Institute of Technology Mandi
Himachal Pradesh, India

LIST OF PUBLICATIONS

This thesis is based on the following publications and manuscripts:

1. **R. Choudhary,** R. Skomski, and A. Kashyap, "Magnetism in Cr_2O_3 Thin Films: An Ab Initio Study" *IEEE Trans. Mag.,* Vol. 51, NO. 11, pp. 2300703, **(2015).**

2. **R. Choudhary**, P. Kumar, P. Manchanda, D. J. Sellmyer, P. A. Dowben, A. Kashyap, and R. Skomski, "Interface-induced spin polarization in graphene on chromia," *IEEE Mag. Lett.,* Vol 7, pp. 1-4, **(2016).**

3. **R. Choudhary**, T. Komesu, P. Kumar, P. Manchanda, K. Taguchi, T. Okuda, K. Miyamoto, P. A. Dowben, R. Skomski and A. Kashyap, "Exchange coupling and spin structure in cobalt-on-chromia thin films," *EPL* , vol. 115, pp. 17003 **(2016)**.

4. **R. Choudhary**, R. Skomski, and A. Kashyap, "Electric-field-controlled interface exchange coupling in cobalt-chromia bilayer film: first principles calculations", IEEE Trans. Magn. , Vol. 53, pp. 7002104 **(2017)**.

5. **R. Choudhary**, R. Skomski, and A. Kashyap, "Electric-field control of magnetism in chromia thin film and graphene on chromia bilayer", *J. Magn. Magn. Mater.*, Vol. 443, pp. 4-8 **(2017).**

The following publications are included in the 'Appendix' of this thesis:

1. **R. Choudhary**, P. Manchanda, A. Enders, B Balamurugan, A. Kashyap, D. J. Sellmyer, E. C. H. Sykes and R. Skomski "Spin-modified catalysis," *J. Appl. Phys.,* Vol. 117, pp. 17D720, **(2015).**

2. **R. Choudhary**, P. Kharel, S. R. Valloppilly, Y. Jin, A. O'Connell, Y. Huh, S. Gilbert, A. Kashyap, D. J. Sellmyer, and R. Skomski, "Structural disorder and magnetism in the spin-gapless semiconductor CoFeCrAl" *AIP Adv.*, Vol.6, pp. 056304, **(2016).**

Another Publication

1. Y. Jin, P. Kharel, S. R. Valloppilly, X.-Z. Li, D. R. Kim, G. J. Zhao, T. Y. Chen, **R. Choudhary**, A. Kashyap, R. Skomski, and D. J. Sellmyer, "Half-metallicity in highly L21-ordered CoFeCrAl thin films," *Appl. Phys. Lett.* , vol. 109, pp. 142410 **(2016).**

Conference Paper:

1. **R. Choudhary**, P. Kumar, P. Manchanda, Y. Liu, A. Kashyap, D. J. Sellmyer, R. Skomski, "Atomic Magnetic Properties of Pt-Lean FePt and CoPt Derivatives", REPM'14-Proceedings of the 23rd International Workshop on Rare Earth Permanent Magnets and their Application, 289, 2014.

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