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Unexpected Spin-flipping in High Magnetic Nano-Fe_3O_4

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Introduction

The search for high resistive soft magnet that coexists of a giant magnetization (>1 T) and high resistivity in a single compound has been intense in recent a year, which is driven by the strong industrial demand for new high-permeability thin films with GHz operating frequencies. One of crucial criterion in this new high resistive soft magnet is the necessity of achieving a higher resistivity than conventional metallic magnets, to limit eddy current screening, while maintaining the high permeability and high saturated magnetization of materials. Among the soft magnetic materials, magnetite (Fe_3O_4) is particular fascinating owing to its superior magnetic properties (half-metallic behaviour and high curie temperature of ~860 K) and it has higher resistivity as compared to metallic iron. Moreover, the earlier experimental have demonstrated magnetization enhancement in FePt and Fe_3O_4 nanocomposite magnets by nanoparticle self-assembly. These intriguing properties of Fe_3O_4 have stimulated us to study this materials system intensively [1,2]. Herng et al. [3] developed the high magnetic and low loss Fe_3O_4 nanomagnet via a stoichiometry breaking and nano-crystals self-assembly techniques in Figure 1.

Figure 1 shows the route to achieve giant magnetization and low loss Fe_3O_4 nanomagnet/ultrathin film via the nano-engineering and self-assembly techniques. Originally, bulk magnetite (Fe_3O_4) has inverted cubic spinel structure (Figure 1a) with tetrahedral A sites occupied by Fe^{3+} cations, whereas octahedral B sites are randomly occupied by Fe^{2+} and Fe^{3+} cations with equal concentrations at room temperature with metallic behaviour. The spin of Fe^{3+} cations at octahedral and tetrahedral sites are aligned antiparallel to each other leading to a net magnetic moment ~471 emu/cm^3 experimentally. The typical resistivity of bulk Fe_3O_4 is ~0.005 Ω-cm. In conventional understandings of Fe_3O_4 magnetism, it is understood that octahedral Fe^{2+} and Fe^{3+} are ferromagnetically coupled through double-exchange. In contrast, the Fe^{3+} ions in tetrahedral and octahedral sites are antiferromagnetically coupled through super-exchange and their moments of $5\mu_B$ cancel each other out. Thus, this leads to magnetic moment of $4\mu_B$ per Fe_3O_4 formula unit, which solely comes from octahedral-Fe^{2+} [4-8].

The continuous thickness reduction into nanometer regime has changed the materials properties tremendously. When the film turns into a nanometre scale regime, there is spin-flipping of valence spin tetrahedral Fe^{3+} in the sub-nanostructured Fe_3O_4 film yielding to the high magnetization. Using soft X-ray magnetic circular dichroism (XMCD) and soft X-ray absorption (XAS) both at Fe $L_{3,2}$- and O K-edge supported by first-principle and charge-transfer multiple calculations, Herng et al. [3] observed anomalous enhancement of double-exchange accompanied with a suppression of super-exchange interactions due to the spin-flipping mechanism via oxygen at grain boundaries in ultrathin Fe_3O_4 films.

These nano-crystals will be self-assembled to form the ultrathin film via various growth techniques. The experimental results showed that these ultrathin films possessed the magnetic moment ~760 emu/cm^3 with its resistivity ~0.1 Ω-cm. Recently, there are number of reports on the unexpected giant magnetism (>800 emu/cm^2) in ultrathin (<5 nm) Fe_3O_4 films, which are distinct from those of classical bulk Fe_3O_4 [4,9-11].

To address these bewildering issues, giant magnetization Fe_3O_4 films of 760 emu/cm^3 and regular Fe_3O_4 (reference sample) were prepared and examined using soft X-ray magnetic circular dichroism (SXMCD) and X-ray absorption spectroscopy (XAS) at Fe $L_{3,2}$- edge and O K-edge. Supported by charge-transfer multiplet and first-principles calculations, Herng et al. [3] revealed that the magnetization enhancement is due to spin-flipping of valence spins in tetrahedral-Fe^{3+}, assisted by oxygen vacancies at grain boundaries.

Series of Fe_3O_4 films with various grain sizes, from ~2.5 to ~17 nm, was grown on glass substrates by pulsed laser deposition (PLD) technique. The films were prepared on glass substrate because lattice mismatch between glass and Fe_3O_4 is favourable for formation of small grain size (higher density of grain boundaries). Grain sizes were determined by high resolution transmission electron microscope (HRTEM) measurements. The film with an average size of 2.5 nm (black loop) exhibited a typical saturation magnetization (M_s) of ~760 emu/cm^3, which is far higher than the value of usual bulk Fe_3O_4, ~471 emu/cm^3. With increasing grain size, the M_s reduced and M_s reached a typical M_s of ~390 emu/cm^3 for the film with grain size of 15 nm (Figure 1b). All films exhibited Verwey transition temperature (T_V), which is a characteristic of Fe_3O_4. The T_V for 2.5 nm (15 nm) grain-sized film was ~105 K (~114 K), which is around the bulk value of 120 K. These observations confimed that films exhibited the Fe_3O_4 charactiristics [4-6].

The XAS and SXMCD revealed that the origin of high magnetization in these films was attributed to the spin flipping of tetrahedral Fe^{3+} cations (~25%) at Fe_3O_4 grain boundary via oxygen, enhancing the overall double-exchange and suppressing the super-exchange interactions. The first-principles calculations successfully explained the experimental data by demonstrating spontaneous spin-flipping of tetrahedral-Fe at (001)-T_dO_h-GB and also appearance of spin moment in nearby oxygen.

This discovery of spin-manipulated magnetism in Fe_3O_4 nanostructure that is large, controllable and stable at room temperature presents new opportunities for fundamental studies of carrier–dopant magnetic exchange interactions in various doped-Fe_3O_4 (or ferrite) material systems. Furthermore, this work may raise possibilities for the development of controllable spin-based information technologies from Fe_3O_4-based or ferrite-based compounds.

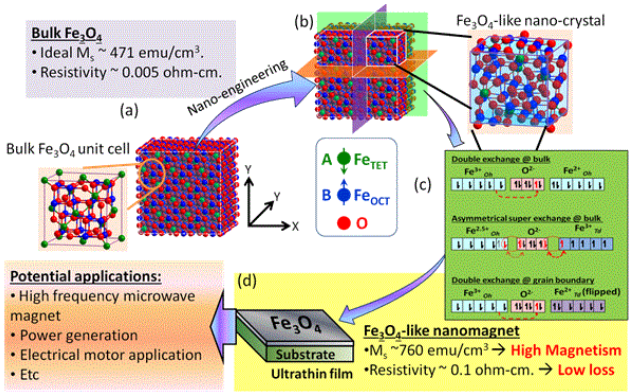

Figure 1: (a) The atomistic model of bulk Fe_3O_4 and its unit cell. The experimental saturated magnetization of bulk Fe_3O_4 is 471 emu/cm^3 with its resistivity of ~0.005 Ω-cm. (b) When the film is getting thinner into sub-nanometer/nomometer scale regime, there is notable change in double exchange and superexchange interaction. (c) The spin flipping of tetrahedral Fe^{3+} cations enhance the double exchange interaction and suppress the superexchange interaction, leading to giant magnetization. (d) These ultrathin films possess the high magnetic moment Tesla and its resistivity has been increased to ~0.1 Ω-cm.

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