Photo-Induced Magnetic Anisotropy due to Coherent Domain Growth

Scott J. Hallock[§], Daniel M. Pajerowski[¥]

[§]Winston Churchill High School, [¥]NIST Center for Neutron Research

Introduction

Photoinduced magnetism refers to physical phenomenon in which the application of visible light to a material causes a change in the magnetization. As an explanation, one can imagine a scenario in which a refrigerator magnet will or will be attracted to steel depending upon whether it had previously been illuminated with red or blue light. Of course, the true practical applications of such a material would be in memory storage and sensing.

Presently, photomagnets as described above only work at cryogenic temperatures, but by better understanding their physical properties, researchers may one day realize room temperature stable materials. One such low-temperature photomagnet is cobalt hexacyanoferrate, $K_jCo_k[Fe(CN)_6]_l \cdot nH_2O$ (where j, k, l, and n can be tuned during synthesis). [1-2]

As thin films are of importance for both optical and magnetic technologies, researchers have found ways to make thin films of the cobalt hexacyanoferrate photomagnet. In 2004, Park *et al.* reported that irradiation of a sequentially adsorbed thin film resulted in an increase of the net magnetization of the system when oriented parallel to an external magnetic field, but a decrease of the net magnetization when oriented perpendicular to the external magnetic field (see Figure 2). [3] In contrast, in 2005, Yamamoto *et al.* reported that irradiation of a Langmuir-Blodgett templated thin film resulted in an increase of net magnetization when oriented parallel to an external magnetic field, with a much smaller increase of net magnetization when oriented perpendicular to the external magnetic field (see Figure 3). [4]

To obtain a deeper understanding of these data, a model must be employed that can explain these observations, and in turn give guidance to further experiments. In this poster, we propose that demagnetizing effects can explain the general phenomenon of photo-induced magnetic anisotropy in coordination polymers. A model will be outlined, and a comparison of model to experimental data will be presented.

Demagnetizing Model

In magnetic materials, the internal magnetic field may be different than the applied field. This internal field may be written to depend only on the shape of the magnetic object and the size of the magnetization:

$$H_{eff} = H_{lab} - \frac{N}{4\pi} M$$

where N is the geometrical demagnetizing factor, M is the magnetization per unit volume, H_{lab} is the applied field, and H_{eff} is the effective field taking into account demagnetization. Magnetic susceptibility is defined as the relationship between magnetization and applied magnetic field, namely

$$M = \chi H_{lab}$$

Based upon these equations, a simple formula for the effective magnetic susceptibility is

$$\chi_{eff} = \frac{\chi}{1+\chi N}$$

The dependence of the effective susceptibility upon the actual susceptibility and the demagnetizing factor is illustrated in Figure 3. In the limit of large susceptibility, the effective susceptibility simply goes inversely proportional to the demagnetizing factor.

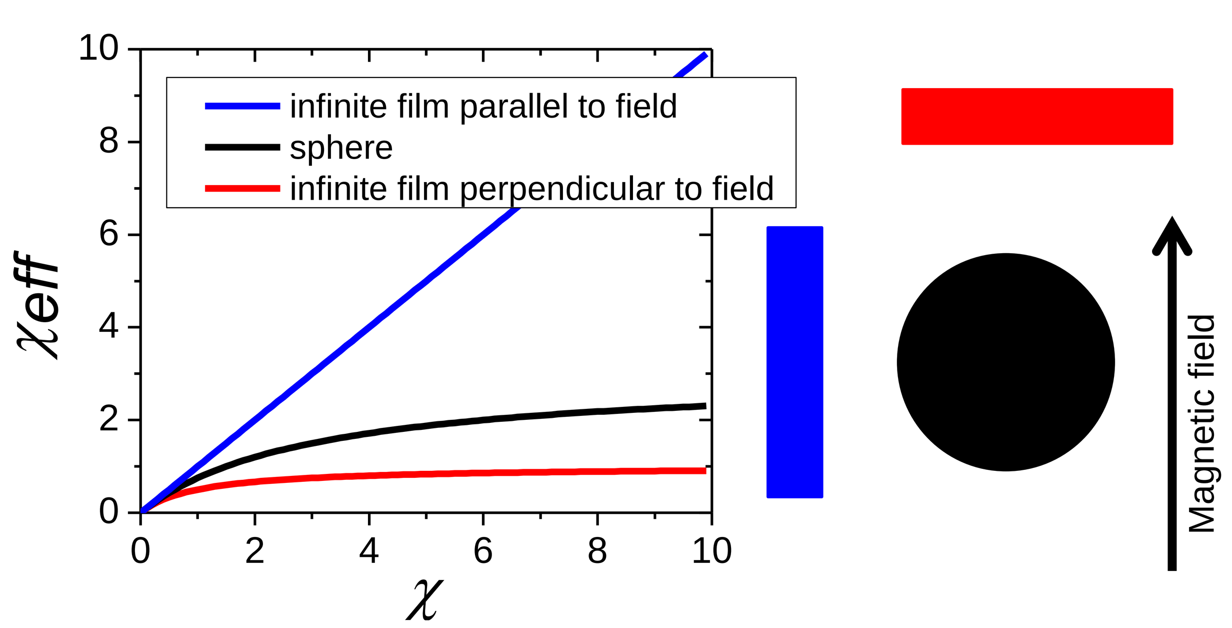


Figure 1. Illustration of the effect of demagnetization on the effective susceptibility for three relevant geometries of high symmetry.

Experimental Data

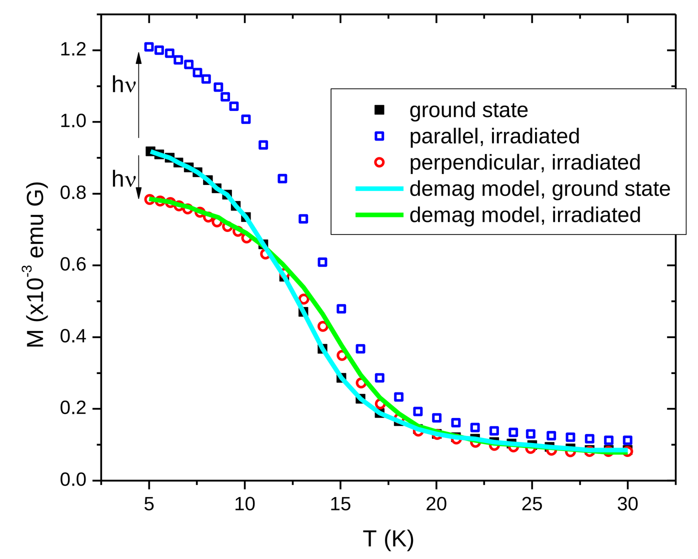


Figure 2. Park *et al.* 2004 observations. Irradiation of a sequentially adsorbed thin film resulted in an increase of the net magnetization of the system when oriented parallel to an external magnetic field, but a decrease of the net magnetization when oriented perpendicular to the external magnetic field.

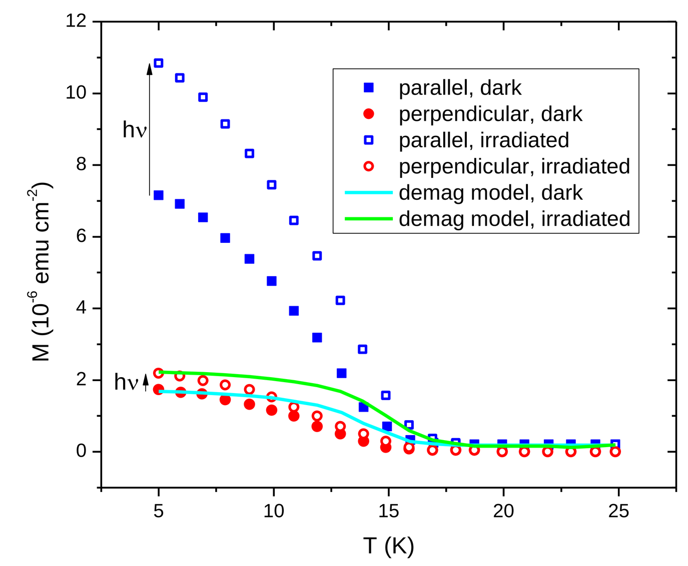


Figure 3. Yamamoto *et al.* 2005 observations. Irradiation of a Langmuir-Blodgett templated thin film resulted in an increase of net magnetization when oriented parallel to an external magnetic field, with a much smaller increase of net magnetization when oriented perpendicular to the external magnetic field

Photodecrease due to Domain Growth

$$\chi_{eff} = \frac{\chi}{1+\chi N} n_{HS} \qquad \chi > 0, n_{HS} \in [0,1], N \in [0,1]$$

If N is not a function of n_{HS} ➔ $N \neq N(n_{HS})$:

$$\frac{\delta\chi_{eff}}{\delta n_{HS}} = \frac{\chi}{1+\chi N} \Rightarrow \frac{\delta\chi_{eff}}{\delta n_{HS}} \geq 0$$

Can't reduce effective susceptibility while increaseing high spin fraction!

Assuming that N is a function of n_{HS} ➔ $N = N(n_{HS})$:

$$\frac{\delta\chi_{eff}}{\delta n_{HS}} = \frac{\chi}{1+\chi N(n_{HS})} - \frac{n_{HS} N'(n_{HS}) \chi^2}{[1+\chi N(n_{HS})]^2}$$

$$\boxed{\frac{\delta\chi_{eff}}{\delta n_{HS}} < 0}$$

$$\frac{\chi}{1+\chi N(n_{HS})} - \frac{n_{HS} N'(n_{HS}) \chi^2}{[1+\chi N(n_{HS})]^2} < 0$$

$$1 - \frac{n_{HS} N'(n_{HS}) \chi}{1+\chi N(n_{HS})} < 0$$

If the demagnetizing factor is increasing as the high spin fraction is increasing, the effective susceptibility can actually be reduced as the high spin fraction increases!

$$\frac{n_{HS} N'(n_{HS}) \chi}{1+\chi N(n_{HS})} > 1$$

$$n_{HS} N'(n_{HS}) \chi > 1 + \chi N(n_{HS})$$

$$1 + \chi N(n_{HS}) - n_{HS} N'(n_{HS}) \chi < 0$$

$$1 < \chi (n_{HS} N' - N)$$

$$n_{HS} N' - N > 0$$

INVESTIGATE FURTHER!!!

$n_{HS}N' > N$ in the limit $n_{HS} \rightarrow 1$ if $N \rightarrow 1$, $\boxed{N' > 1}$

Finite Element Analysis with FiPy

FiPy is a free, Python based finite element solver package developed in the Center for Theoretical and Computational Materials Science (CTCMS) right here at NIST.[8] We used FiPy to calculate the magnetic scalar potential and magnetic field vectors given a distribution of magnetic charges. These magnetic charges are not real in the way electrons and protons are real, but rather come out of the theory for magnetostatics in the regime without free electric current. In fact, there is a very distinct parallel between magnetostatics and electrostatics in this limit. As such, to test the accuracy of our code, we first tested the well known case of a parallel plate capacitor in one, two, and three dimensions. An example of a 2-d solution is shown in Figure 5, and the numerical results agreed with the well known analytical solution.

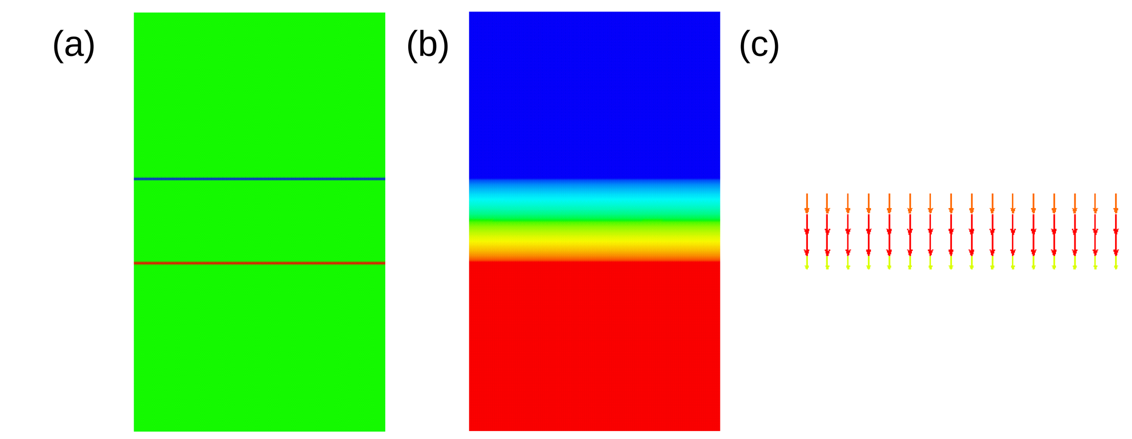


Figure 5. Parallel plate capacitor in 2-d. (a) Charge distribution with blue being positive and red being negative charge, (b) electric potential, and (c) electric field represented by vectors.

Modeling Experimental Data

The demagnetizing model may be used to calculate the perpendicular orientations of the photomagnetic thin films as a function of parallel orientations.

To begin, the Langmuir-Blodgett templated film is considered. The structure consists of disordered mono-layers of cobalt hexacyanoferrate separated by templating materials, Figure 4 (a). Therefore, both before and after photoirradiation, the magnet is in a highly two dimensional film that can very nearly be approximated by the infinite film model. A good agreement is found between experimental data of the perpendicular orientation of the film and the demagnetization model, Figure 1.

To understand the sequentially adsorbed film, it is necessary to have a more complicated model motivated by experimental observation of coherent magnetic domain growth under photoirradiation. Both AC-susceptibilty measurements [4], and x-ray diffraction measurements [3, have shown that the size of magnetic clusters within cobalt hexacyanoferrate materials grows due to interactions between neighboring ions in the material, which are energetically favorable to be in similar states. This growing of clusters with photoirradiation is schematized in Figure 4 (b) and (c). As sequentially adsorbed films are in the range of 100 nm, [2] as are the saturation size of the magnetic clusters [5], these coherent domain growth effects must be considered, Figure 4 (d), (e), and (f). The experimental data may be reproduced if the ground state consists of isolated clusters similar to spheres, and the photoirradiated state is anisotropic in shape similar to infinite planes or anisotropic ellipsoids, Figure 4 (f).

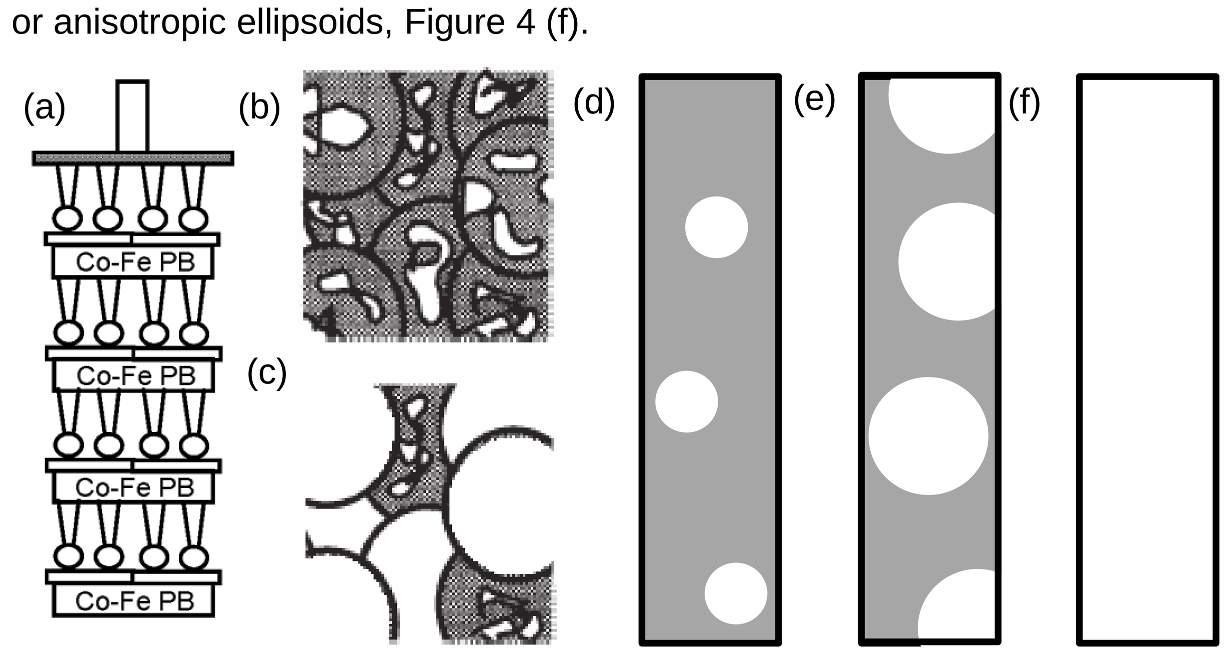


Figure 4. Film morphologies. (a) The disordered mono-layers of cobalt hexacyanoferrate separated by templating materials for the Langmuir-Blodgett film. (b), (c) schematization of growing of clusters with photoirradiation (d), (e), (f) isolated clusters of magnetic domain grow to a shape similar to infinite planes.

Modeling the Magnetic Drops: Crossover Between 3-d and 2-d Behavior

In order to flesh out the model displayed in Figures 2 and 3, numerical calculations of demagnetizing factors for growing magnetic domains were performed. The model used periodic boundary conditions in all directions, with ample spacing along the z-direction to approximate isolated films. Magnetic drops were approximated as cubes, which grow in size until the entire film is magnetic, Figure 6. Demagnetizing factors were solved for by taking the average magnetic field magnitude within the magnetic region, and a dependence of the demagnetizing factor upon the high-spin fraction (n_{HS}) was calculated, Figure 7.

Figure 7. The demagnetizing factor as a function of the high-spin fraction. The data was obtained with FiPy using the simple cube geometry for the drops.

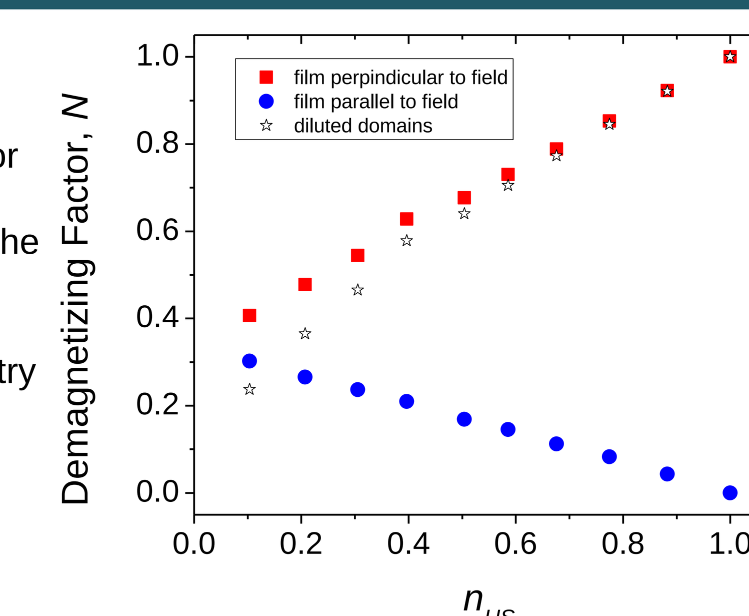
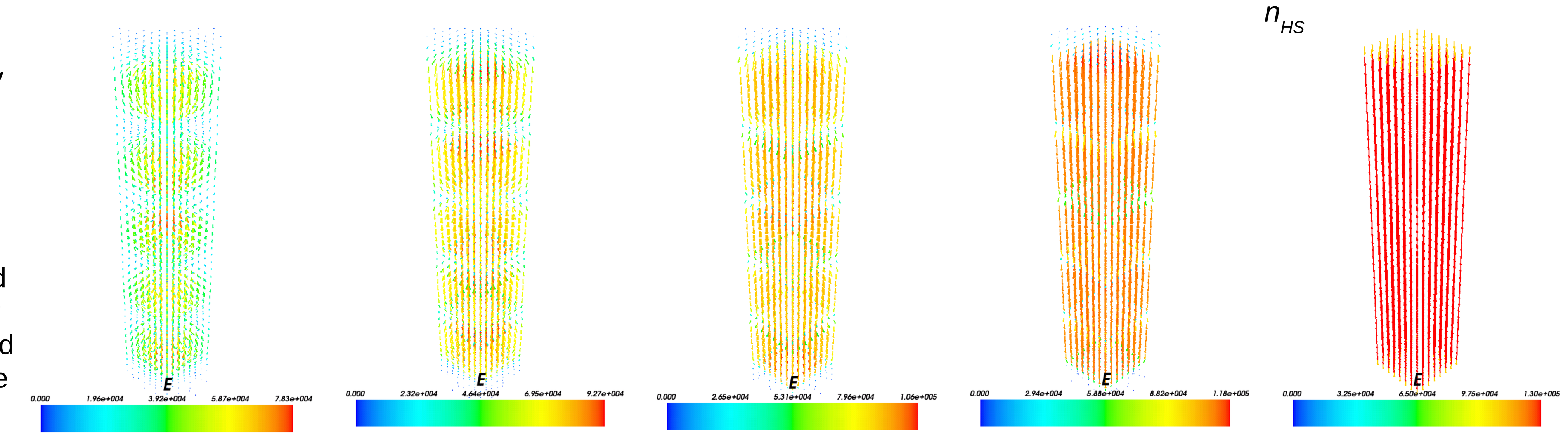


Figure 6. Magnetic field represented by vectors in 3-d space. In each model moving from left to right, the cubic magnetic domain is increased in size until the limit of a fully magnetized film is reached a the far right.



Conclusions and Ongoing Work

The demagnetizing model can, for the most part, explain the phenomenon of photo-induced magnetic anisotropy. Specifically, the surprising decrease in low-field magnetization for sequentially adsorbed thin films, and the reduced magnitude of the photoeffect for templated films. Currently work is underway to utilize more physical spherical magnetic droplets using the coding framework that was developed of the summer to quantitatively model the effect.

Acknowledgements

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