Anisotropic photoinduced magnetism of a Rb$_{j}$Co$_{k}$[Fe(CN)$_{6}$]$_{l}$·nH$_{2}$O thin film

J.-H. Park$^{a}$, E. Čižmár$^{b}$, and M. W. Meisel

Department of Physics and the Center for Condensed Matter Sciences, University of Florida, Gainesville, FL 32611-8440

Y. D. Huh$^{c}$, F. Frye, S. Lane, and D. R. Talham

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200

(Dated: November 6, 2017)

Abstract

A magneto-optically active thin film of Rb$_{j}$Co$_{k}$[Fe(CN)$_{6}$]$_{l}$·nH$_{2}$O has been prepared using a sequential assembly method. Upon irradiation with light and at 5 K, the net magnetization of the film increased when the surface of the film was oriented parallel to the external magnetic field of 0.1 T. However, when the surface of the film was perpendicular to the field, the net magnetization decreased upon irradiation. The presence of dipolar fields and the low-dimensional nature of the system are used to describe the orientation dependence of the photoinduced magnetization. The ability to increase or decrease the photoinduced magnetization by changing the orientation of the system with respect to the field is a new phenomenon that may be useful in future device applications.
The magnetic properties of thin films can be different from those of bulk materials and may exhibit anisotropy originating from the low-dimensional character of the systems. The high surface to volume ratios of thin films are often advantageous in magneto-optical studies since more photons can interact with the system without being attenuated. We adopted a sequential assembly method to generate a magnetic, optically-controllable, thin film based on a Prussian blue analogue, a class of molecular magnets consisting of octahedral \([M(CN)_6]^n−\) complexes bridged through metal ions. In this letter, we report the first example of a thin film in which an increase or decrease of the photoinduced magnetization was controlled by the orientation of the system with respect to the applied magnetic field.

A sequential synthesis protocol was used to generate a thin film whose general chemical formula was \(Rb_jCo_k[Fe(CN)_6]_l\cdot nH_2O\). The substrate, a mylar sheet (thickness \(\sim 100 \mu m\)), was repeatedly immersed, for 20 cycles, in a \(5 \times 10^{−3} \) M aqueous solution of cobalt(II) nitrate and then in a mixed solution of \(2 \times 10^{−2} \) M potassium ferricyanide and \(1.25 \times 10^{−2} \) M rubidium nitrate. The metal ratios used to prepare the film yield bulk samples with formula \(Rb_{1.8}Co_4[Fe(CN)_6]_3\cdot 13H_2O\). While the composition of the film has not yet been chemically confirmed, the magneto-optical properties, which in this series are very sensitive to composition, are consistent with this approximate formula. Based upon atomic force microscope (AFM) and scanning electron microscope (SEM) studies, the film was determined to be continuous and to have an average thickness of about 200 nm and roughness of 50 nm. The resulting film was cut into squares and stacked into a polycarbonate sample holder. A bundle of optical fibers was introduced to the stacked films and connected to a room temperature halogen light source. Using a commercial superconducting quantum interference device (SQUID) magnetometer, the magnetization of the sample was investigated from 5 K to 300 K and in fields up to 7 T.

The photoinduced magnetism in Prussian blue analogues has been extensively studied over the last decade, and the family of cobalt hexacyanoferrate was one of the first examples in which the diamagnetic to ferrimagnetic transition was observed upon irradiation with visible light. More specifically, in its dark state, the bulk compound \(Rb_jCo_k[Fe(CN)_6]_l\cdot nH_2O\) contains a mixture of two dominant spin configurations below \(T_C \sim 20 K\), see Table 1. The relative population of each state can be controlled by chemically tuning the \(Co/Fe\) ratio of the sample. Upon irradiation with light, an electron from the Fe\(^{II}\)(LS, \(S = 0\)) ion transfers to the Co\(^{III}\)(LS, \(S = 0\)) ion within the diamagnetic...
sites, creating a ferrimagnetic spin state, namely Fe$^{III}$(LS, $S = 1/2$)–CN–Co$^{II}$(HS, $S = 3/2$), Table 1. In other words as a consequence of the irradiation, the net magnetization of the compound increases, and the metastable Fe$^{III}$(LS)/Co$^{II}$(HS) state is maintained as long as the sample is kept below approximately 150 K.

The photoinduced increase of the magnetization of our film is shown in Fig. 1(a), and this effect was observed when the surface of the film was parallel to the external magnetic field ($H_E \parallel \text{film}$) of 0.1 T. This observation is consistent with the measurements made on bulk powdered samples. However, under the same experimental conditions (i.e. the sample was field-cooled to 5 K with $H_E = 0.1$ T, and then subsequently exposed to light), the net magnetization decreased when the film was oriented perpendicular to the field ($H_E \perp \text{film}$), as shown in Fig. 1(c).

The anisotropy of these magneto-optical effects was sustained in the temperature dependences of the field-cooled (fc) and zero-field-cooled (zfc) magnetizations, see Figs. 1(b) and 1(d). In both orientations, the divergences between the zfc and fc magnetizations are consistent with cluster spin-glass behavior and indicate the existence of interacting ferrimagnetic domains. As a result of photoinduced spin creation, the temperature where the zfc magnetization achieves its maximum value has shifted towards higher temperatures, and this behavior can be described as an increase in the size of the spin clusters. This argument also explains the photoinduced increase of $T_C$ when $H_E \parallel \text{film}$, Fig. 1(b). When $H_E \perp \text{film}$, Fig. 1(d), the photoinduced increase of $T_C$ is more subtle, as it competes with cluster spin-glass effects.

The anisotropy of the magneto-optical properties of our film arises from an interplay between the low-dimensional nature of the system and the dipolar magnetic fields generated by the ferrimagnetic domains. This interactive relationship is shown schematically in Fig. 2, for the case where $H_E \perp \text{film}$. When the sample is cooled from room temperature to below $T_C$, the primordial spin configurations consist of ferrimagnetic domains surrounded by diamagnetic regions, Fig. 2(a). This arrangement arises from the random distribution of the local chemical composition of the film. However, structural order is maintained at least of the size of the magnetic coherence length, since the $T_C$ values we observe are close to the bulk value of $\sim 21$ K. It is important to emphasize that the primordial ferrimagnetic domains possess net magnetic moments which have been aligned parallel to $H_E$. Consequently, the net magnetic field acting on the diamagnetic sites is the vector sum of

\[ H_{\text{net}} = H_E \]
the external magnetic field ($H_E$) and the dipolar field ($H_D$), where $H_D$ is antiparallel to $H_E$. When illuminated, the diamagnetic site will become ferrimagnetic, and the direction of the photoinduced magnetization will follow that of the net field as shown in Fig. 2(b) (where the $H_D > H_E$), and Fig. 2(c) (where the $H_D < H_E$). As a result, the net magnetization of the film in the photoinduced state decreases when $H_D > H_E$, and this expectation is consistent with our result for the photoinduced decrease of the magnetization as shown in Figs. 1(c) and 1(d). When $H_D < H_E$ as shown in Fig. 2(c), the net magnetization is expected to increase, and this effect was observed experimentally at $H_E = 7$ T, see Fig. 2(d).

For $H_E \parallel$ film, the net moments of the primordial ferrimagnetic domains align with $H_E$. Consequently, due to the two-dimensional nature of the film, the diamagnetic sites experience a net magnetic field which is always in the direction of $H_E$, and the magneto-optically induced diamagnetic to ferrimagnetic conversion results in a global increase in the total magnetization, Figs. 1(a) and 1(b).

In summary, using a sequential assembly method, we synthesized a magneto-optically active thin film of $\text{Rb}_j\text{Co}_k[\text{Fe(CN)}_6]_l\cdot n\text{H}_2\text{O}$. Below $T_C \sim 20$ K when the film was placed parallel to the external magnetic field, the net magnetization increased upon irradiation with light. However, when the film was oriented perpendicular to the external field, the net magnetization in the photoinduced state decreased. The anisotropy of these magneto-optical properties arises from an interplay between the low-dimensional nature of the system and the dipolar fields. The ability to increase or decrease the photoinduced magnetization by changing the orientation of the system with respect to the field is a new phenomenon, heretofore not observed in magnetic thin films, and provides a novel mechanism that may be useful in future device applications.

This work was supported, in part, by NSF DMR-9900855 (DRT), NSF DMR-0113714 (MWM and DRT), ACS-PRF 36163-AC5 (MWM and DRT), NSF DGE-0209410 (EC), and NSF DMR-0305371 (MWM). We gratefully acknowledge early contribution from J. T. Culp.
a) Electronic mail: juhyun@phys.ufl.edu

b) Current address: Institute of Physics, Faculty of Science, P. J. Šafárik University, Košice, Slovakia.

c) Current address: Department of Chemistry, Dankook University, Seoul, Korea.

1 A. Goujon, O. Roubeau, F. Varret, A. Dolbecq, A. Bleuzen, and M. Verdaguer, Eur. Phys. J. B 14, 115 (2000).

2 M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, and F. Villain, Coord. Chem. Rev. 190-192, 1023 (1999).

3 J. T. Culp, J.-H. Park, I. O. Benitez, Y. D. Huh, M. W. Meisel, and D. R. Talham, Chem. Mater. 15, 3431 (2003).

4 J. T. Culp, J.-H. Park, I. O. Benitez, M. W. Meisel, and D. R. Talham, Polyhedron 22, 2125 (2003).

5 A. Bleuzen, C. Lomenech, V. Escax, F. Villain, F. Varret, C. Cartier dit Moulin, and M. Verdaguer, J. Am. Chem. Soc. 122, 6648 (2000).

6 V. Escax, A. Bleuzen, C. Cartier dit Moulin, F. Villain, A. Goujon, F. Varret, and M. Verdaguer, J. Am. Chem. Soc. 123, 12536 (2001).

7 M. Verdaguer, Science 272, 698 (1996).

8 O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science 272, 704 (1996).

9 K. Yoshizawa, F. Mohri, G. Nuspl, and T. Yamabe, J. Phys. Chem. B 102, 5432 (1998).

10 O. Sato, Y. Einaga, A. Fujishima, and K. Hashimoto, Inorg. Chem. 38, 4405 (1999).

11 D. A. Pejaković, J. L. Manson, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. 85, 1994 (2000).

12 C. Cartier dit Moulin, F. Villain, A. Bleuzen, M.-A. Arrio, P. Sainctavit, C. Lomenech, V. Escax, F. Baudelet, E. Dartyge, J. J. Gallet, and M. Verdaguer, J. Am. Chem. Soc. 122, 6653 (2000).

13 G. Champion, V. Escax, C. Cartier dit Moulin, A. Bleuzen, F. Villain, F. Baudelet, E. Dartyge, and M. Verdaguer, J. Am. Chem. Soc. 123, 12544 (2001).

14 T. Kawamoto, Y. Asai, and S. Abe, Phys. Rev. Lett. 86, 348 (2001).

15 F. Varret, M. Nogues, and A. Goujon in Magnetism: Molecules to Materials I, edited by
16 S. Ohkoshi and K. Hashimoto, J. Photochem. Photobiol. C 2, 71 (2001).

17 H. Tokoro, S. Ohkoshi, and K. Hashimoto, Appl. Phys. Lett. 82, 1245 (2003).

18 M. Hanawa, Y. Moritomo, A. Kuriki, J. Tateishi, K. Kato, M. Takata, and M. Sakata, J. Phys. Soc. Jpn. 72, 987 (2003).

19 J.-H. Park, Y. D. Huh, E. Čížmár, S. J. Gamble, D. R. Talham, and M. W. Meisel. J. Magn. Magn. Mater. 272-276, 1116 (2004).

20 The choice of field-cooling instead of zero-field-cooling was made to maximize the magnetization along the external field and to minimize the variation of the magnetization due to the irreversible temperature dependence of the zero-field-cooled magnetization, an effect which is a common characteristic of a spin-glass.
TABLE I: Spin configurations of Rb$_j$Co$_k$[Fe(CN)$_6$]$_l$·$n$H$_2$O when $T < T_C$.

| States          | Spin Configurations $^a$                                      |
|-----------------|---------------------------------------------------------------|
| Diamagnetic     | Fe$^{II}$(LS, $S = 0$)–CN–Co$^{III}$(LS, $S = 0$)             |
| Ferrimagnetic   | Fe$^{III}$(LS, $S = 1/2$)–CN–Co$^{II}$(HS, $S = 3/2$)         |

$^a$LS = low spin and HS = high spin.
FIG. 1: Time and temperature dependences of the magnetization of photoinduced (light) and dark states, when the external magnetic field is parallel to the film (a, b) and perpendicular to the film (c, d).

FIG. 2: Schematic description of the spin configurations of the domains in the film when \( H_E \bot \) surface, where \( H_E \) is in the \( +\hat{z} \) direction. Here, the clear and the shaded arrows represent \( \text{Co}^{II}(HS, S = 3/2) \) and \( \text{Fe}^{III}(LS, S = 1/2) \) respectively. In (a), the primordial ferrimagnetic domains coexist with diamagnetic regions when cooled to \( T < T_C \) before irradiation. The net magnetic field on the diamagnetic site is a vector sum of the external magnetic field (\( H_E \)) and the dipolar field (\( H_D \)) produced by the ferrimagnetic domains. In (b), at \( T < T_C \) and \( H_D > H_E \), the diamagnetic regions are magneto-optically converted to ferrimagnetic ones, and the newly formed ferrimagnetic net moments point in the \( -\hat{z} \) direction, resulting in a decrease of the net magnetization. In (c), the photoinduced ferrimagnetic net moments point \( +\hat{z} \) direction since \( H_D < H_E \), and in this case, the net magnetization increases in the photoinduced state, as observed experimentally when \( H_E = 7 \) T, see (d).
Figure 1. J.-H. Park, Applied Physics Letters.
Figure 2. J.-H. Park, Applied Physics Letters.