External Magnetic Field Effect on the Photoinduced Magnetization in a Cobalt Iron Cyanide

Yasuaki Einaga,[†] Shin-ichi Ohkoshi,[††] Osamu Sato,[†††] Akira Fujishima,*[†,†††] and Kazuhito Hashimoto*[††,†††]
[†]*Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*
[††]*Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904*
[†††]*Kanagawa Academy of Science and Technology, in Tokyo Institute of Polytechnics, Atsugi, Kanagawa 243-0297*

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We studied the external magnetic field effects on the photoinduced magnetization of a cobalt iron cyanide, $K_{0.4}Co_{1.3}[Fe(CN)_6]\cdot 5H_2O$. Photoinduced magnetization value was increased ca. 20 % at maximum under the magnetic field of 50000 G at 5 K. In addition, in the ferrimagnetic region ($T < T_c$ = 26 K), the external magnetic field accelerated the rate of photo-induced spin generation. Those data suggest that external magnetic field increases magnetic interaction between the excited state and spin clusters.

The design of molecule-based compounds has been attracting attention in the field of magnetism.[1-4] One of the challenging issues in this field is to control the magnetic phase transition by external stimuli (pressure, temperature, light, etc.). We have reported that magnetization is changed by electrochemical redox reactions in chromium cyanide.[5,6] We have also reported a reversible photoinduced magnetization at low temperature [7,8] and cation driven electron transfer involving a spin transition around room temperature [9] using a cobalt iron cyanide ($K_{0.4}Co_{1.3}[Fe(CN)_6]\cdot 5H_2O$) thin film, which was synthesized via electrochemical route. We therefore could control the magnetic property reversibly by optical,[7,8] chemical,[9] and electrochemical perturbations. Here, we tried to control the photoinduced magnetization by an external magnetic field. In this paper, we report the magnetic field effect on the photoindeced magnetization of the cobalt iron cyanide.

The cobalt iron cyanide thin film (ca. 0.05 ~ 0.1 μm thickness) was synthesized on a Pt electrode under potentiostatic condition at - 0.4 V versus Saturated Calomel Electrode (SCE) in an aqueous solution containing 0.5 mmol dm^{-3} $K_3Fe^{III}(CN)_6$, 0.5 mmol dm^{-3} $Co^{II}(NO_3)_2$ and 1 mol dm^{-3} $NaNO_3$. Magnetic properties were investigated at 5 K and 30 K with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). An excitation light (He-Ne laser, 633.0 nm, 5.0 mW/cm^2) was guided by an optical fiber to the sample set in the SQUID.

The photoinduced magnetization of this compound is due to the change of the electronic states by light illumination, resulting that unpaired electron spins are generated on the metal ions, i.e., $Co^{III}(t_{2g}{}^6, S=0)$-NC-$Fe^{II}(t_{2g}{}^6, S=0)$ —> $Co^{II}(t_{2g}{}^5e_g{}^2, S=2/3)$-NC-FeIII($t_{2g}{}^5$, S=1/2).[10]

Figure 1 shows the changes of the photo-induced magnetization value (ΔM) irradiated in the presence of weak (5 G, ●) and strong external magnetic field (50000 G, ○) at 5 K. The irradiation was always performed at 5 K in the presence of either weak or strong external magnetic field and then the magnetization values were measured at 50000 G. At the early stage of irradiation ΔM values at 50000 G were ca. 10 % larger than those irradiated at 5 G. However, ΔM values irradiated at 5 G and 50000 G were almost the same after ΔM value reached the saturated one (after more than ca. 120 min irradiation), indicating that the external magnetic field does not affect the final spin alignment but changes the rate of the photoinduced reaction process.

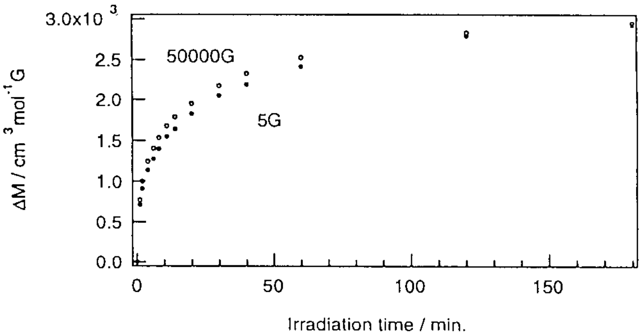

Figure 1. The photo-induced magnetization value measured at 50000 G. The photo-irradiation was performed at 5 G (●) and 50000 G (○). All the experiments were done at 5 K.

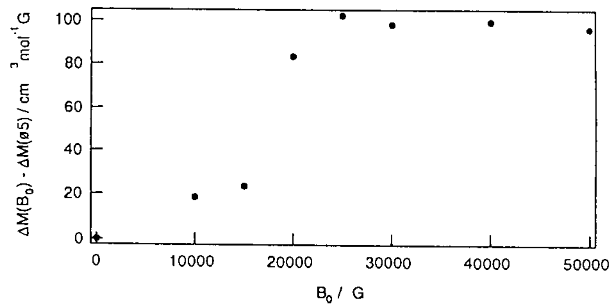

Figure 2. The increased magnetization values after 60 min irradiation as a function of external magnetic field during the irradiation. $\Delta M(B_0)$ and $\Delta M(\varnothing 5)$ represent the photo-induced magnetization values irradiated at the magnetic field of B_0 and 5 G, respectively.

In Figure 2 were plotted the increased photomagnetization value by the external magnetic field (B_0), $\Delta M(B_0)$-$\Delta M(\varnothing 5)$, observed after the irradiation of 60 min as a function of B_0. Here, $\Delta M(B_0)$ and $\Delta M(\varnothing 5)$ represent photo-increased magnetizations irradiated in the presence of external magnetic field of B_0 and 5 G, respectively. At low field, $\Delta M(B_0)$-$\Delta M(\varnothing 5)$ increased gradually and then drastically increased around 15000 G. It seems to be saturated above 20000 G.

In order to estimate the amount of generated spins in this system, the magnetic susceptibilities of the compounds illuminated at 30 K and 5 K were measured. The data are summarized in Table 1.[11] At 30 K, the spin states are paramagnetic and the magnetic interactions between spins are very weak compared to 5 K. Hence the magnetization value is a reflection of the number or spins. The magnetizations at 5 G and at 50000 G were almost the same (Table 1 (b)(c)). This indicates the external magnetic field does not influence the spin formation

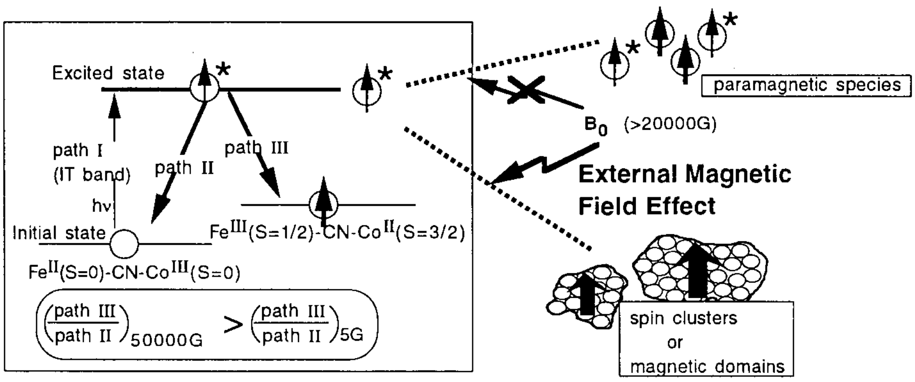

Figure 3. Possible reaction scheme. See text.

in the paramagnetic region. Conversely, when it was illuminated at 5 K below T_C, the difference between magnetization values were much larger (Table 1 (d)(e)), showing that the spin numbers were increased by the external magnetic field in the ferrimagnetic region.

Table 1. Magnetization values which reflect the relative spin number. All the values were measured at 30 K (above T_C) at 50000 G. The sequences were as follows;
1) measured at 50000 G (before irradiation) $^{(a)}$—> irradiated at 5 G —> measured at 50000 G $^{(b)(d)}$. 2) measured at 50000 G (before irradiation) $^{(a)}$—> irradiated at 50000 G —> measured at 50000 G$^{(c)(e)}$.

		Before irradiation	After irradiation at 5G	After irradiation at 50000 G
Magnetization at 30 K M (cm^3mol^{-1})	Irradiated at 30K	658 (a)	1028 (b)	1036 (c)
	Irradiated at 5K	658 (a)	1035 (d)	1083 (e)

One of the possible reaction schemes is schematically shown in Figure 3. The ground state Fe^{II}-CN-Co^{III} is pumped to an excited state by photo-irradiation (path I). The excited state may relax to either the initial Fe^{II}-CN-Co^{III} state (a deactivation process: path II) or the final $Fe^{III}(S=1/2)$-CN-$Co^{II}(S=3/2)$ state (an electron-transfer process: path III). The external magnetic field perturbs the kinetic ratio of the path II and the path III. The results that the spin numbers were increased by external magnetic field only in the ferrimagnetic region suggests that the external magnetic field affects not the magnetic interaction between the excited state and paramagnetic spins but magnetic interaction between the excited state and the ordering spin groups such as spin clusters and magnetic domains.

Instead of the excited state, an alternative metastable state relaxed from the excited state can play the same role in the above model. In any case, spin clusters contribute to this magnetic field effect. We expect that the photoexcited species are spatially adjacent to the magnetic domains. If our model is correct, cooperative behavior should be expected in this system. We are investigating along this line.

Although various types of magnetic field effects have already been reported,[12-21] their effects are due to the interaction among unpaired electrons of molecules, ex., radical pair mechanism, Δg mechanism. In our system, however, the external magnetic field affects magnetic interaction between the excited state and the ordering spin groups such as spin clusters and magnetic domains. We believe that this type of magnetic field effect is a novel one and opens a new avenue in the field of magnetic field effects.

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11 Because the sample was a thin film and the background magnetization value of substrate were included in those figures, the measured magnetization values are meaningful only when compared relatively.
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