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Photoinduced Magnetization of a Cobalt–Iron Cyanide

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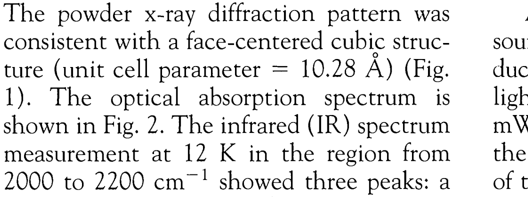
Photoinduced magnetization was observed in a Prussian blue analog, $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$. An increase in the critical temperature from 16 to 19 kelvin was observed as a result of red light illumination. Moreover, the magnetization in the ferrimagnetic region below 16 kelvin was substantially increased after illumination and could be restored almost to its original level by thermal treatment. These effects are thought to be caused by an internal photochemical redox reaction. Furthermore, blue light illumination could be used to partly remove the enhancement of the magnetization. Such control over magnetic properties by optical stimuli may have application in magneto-optical devices.

The design of molecule-based compounds exhibiting spontaneous magnetization with high critical temperature, T_c, is one of the main challenges in molecular materials science. Compelling results have recently been reported (*1–11*). Current research in this field aims not only to improve magnetic properties, but also to achieve unusual properties, which to date have not been realized in magnets. Our objective is the production of magnets with magnetic properties that can be controlled by external stimuli (Fig. 1). We previously reported an electrochemically tunable molecule-based magnet (*12*). Another possibility is the induction of a magnetic phase transition by optical stimuli. This subject is of considerable importance because the photon mode allows access to a variety of different types of materials with high speed and superior resolution. We now report photoinduced magnetization changes observed in a cobalt–iron cyanide.

A photoinduced memory effect can be triggered by an electronic excitation in a given material that induces the rearrangement of the lattice, resulting in the formation of a new phase after relaxation (*13*). This new phase may have modified magnetic properties. The material we chose in our experiments was a cobalt–iron cyanide–based Prussian blue analog. A compound with a stoichiometry of $Co^{II}_3[Fe^{III}(CN)_6]_2$ (T_c = 14 to 15 K) has already been reported (*14–17*). The reaction of $K_3Fe^{III}(CN)_6$ and $Co^{II}Cl_2$ in aqueous solution produces a dark purple precipitate (*18*). Elemental analysis yields the formula $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$ (*19*), hereafter designated as compound 1. The powder x-ray diffraction pattern was consistent with a face-centered cubic structure (unit cell parameter = 10.28 Å) (Fig. 1). The optical absorption spectrum is shown in Fig. 2. The infrared (IR) spectrum measurement at 12 K in the region from 2000 to 2200 cm^{-1} showed three peaks: a strong peak at 2162 cm^{-1}, a weak peak at 2116 cm^{-1}, and a shoulder at 2097 cm^{-1}. The CN stretch for $Co^{II}_3[Fe^{III}(CN)_6]_2$ was observed at 2160 cm^{-1}, whereas that for $Co^{II}_2[Fe^{II}(CN)_6]$ was observed at 2085 cm^{-1} (*16*). The peak at 2116 cm^{-1} appears when K^+ is included in the compounds. Thus, we think that the peak at 2162 cm^{-1} is due to the stretching of CN in Fe^{III}-CN-Co^{II} links at positions where no K^+ ion is located in interstitial sites, and the peak at 2116 cm^{-1} can be assigned to the stretching of CN groups that surround K^+ ions. The relatively low frequency of the CN stretch (2116 cm^{-1}) indicates that the oxidation states of the metals in Fe-CN-Co moieties exhibiting this frequency can be expressed as Fe^{II}-CN-Co^{III}. The peak at 2097 cm^{-1} is probably due to the CN stretch of Fe^{II}-CN-Co^{II} moieties, but this is not clear at present. Magnetic properties were investigated with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). The product of the molar magnetic susceptibility and temperature, $\chi_M T$, versus T plot first decreased upon cooling and then increased at lower temperatures, indicating a short-range antiferromagnetic interaction between paramagnetic centers bearing different numbers of unpaired electrons (ferrimagnetism). The χ_M^{-1} versus T plots became almost linear in the paramagnetic region below 150 K. The Curie constant, C, and the Weiss constant, θ, were 3.4 $cm^3\ mol^{-1}$ K and −8 K, respectively. The field-cooled magnetization (FCM) versus temperature plots at H = 5 G displayed an abrupt break at T_c = 16 K. The field dependence of the magnetization yielded a magnetization at 5 T of about 2.2 Bohr magnetons per $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$ moiety.

A Hg-Xe lamp was used as the light source in the investigation of the photoinduced magnetic effects. The filtered red light (660 nm with 50-nm half-width, 3.5 mW/cm^2) was guided by optical fiber into the SQUID magnetometer for illumination of the sample. Upon irradiation at 5 K, the magnetization at 5 G increased rapidly and then gradually saturated after several tens of minutes (*20*). The enhancement effect persisted for periods of several days at 5 K. The FCM was measured as a function of temperature before and after light illumination at 5 K (Fig. 3). The T_c after the irradiation was about 19 K, which was 3 K higher than the T_c of the material before illumination. Furthermore, the magnetization was substantially enhanced in the entire temperature



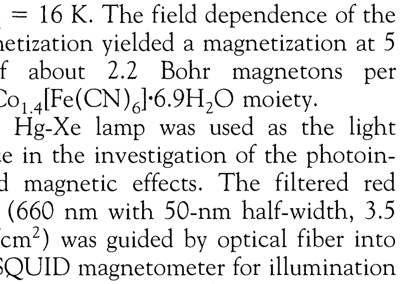


Fig. 1 (left). (**A**) Control of spins in magnetic materials. (**B**) Unit cell of compound 1. Interstitial K^+ ions, water molecules, and defects in the unit cell have been omitted for clarity. **Fig. 2 (right).** Optical absorption spectrum of compound 1.

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range below T_c. Magnetic hysteresis loops were obtained at 5 K before and after the irradiation (Fig. 4). The hysteresis before irradiation yielded a remnant magnetization, M_r, of 2200 cm^3 mol^{-1} G and a coercive field, H_c, of 800 G, whereas the hysteresis loop after the irradiation yielded an M_r value of 3650 cm^3 mol^{-1} G and an H_c value of 1500 G. The magnetization at 5 T was enhanced 1.1 times. The magnetic properties of the illuminated sample relaxed to the initial state when the temperature of the sample was increased to 150 K, showing that the magnetization can be induced by the photon mode and can be restored almost to its original level repeatedly by thermal treatment.

The change in magnetization was also investigated in the paramagnetic region. Similar light-induced phenomena (enhanced magnetization) were observed above T_c. The number of effective spins was increased by red light irradiation. The IR spectrum at 12 K showed that, after red light illumination, the intensity of the peak at 2116 cm^{-1} decreased substantially and that at 2162 cm^{-1} increased. After illumination, the strong peak at 2162 cm^{-1} and small peak at 2097 cm^{-1} remained (*21*). This finding indicates that Fe^{II}-CN-Co^{III} moieties are responsible for the photoinduced effects. On the basis of these results, we conclude that the oxidation states of Fe and Co change from Fe^{II}-CN-Co^{III} to Fe^{III}-CN-Co^{II} by red light irradiation. In general, Co^{II} and Co^{III} coordinated octahedrally by nitrogen have high-spin ($t_{2g}^5e_g^2$, $S = 3/2$) and low-spin (t_{2g}^6, $S = 0$), respectively. Thus, the contribution of the state of Fe^{II}(t_{2g}^6, $S = 0$)-CN-Co^{III}(t_{2g}^6, $S = 0$) is much reduced and that of the state of Fe^{III}(t_{2g}^5, $S = 1/2$)-CN-Co^{II}($t_{2g}^5e_g^2$, $S = 3/2$) is increased by red light irradiation. The increase of the contribution of the paramagnetic components, Fe^{III}(t_{2g}^5, $S = 1/2$) and Co^{II} ($t_{2g}^5e_g^2$, $S = 3/2$), results in an enhancement of the magnetization value. Furthermore, the exchange pathways, which are broken as a result of the diamagnetic character of Fe^{II} (t_{2g}^6, $S = 0$) and Co^{III} (t_{2g}^6, $S = 0$) before illumination, are reestablished by red light irradiation. The T_c value is thus raised because of the increase in the number of magnetic neighbors.

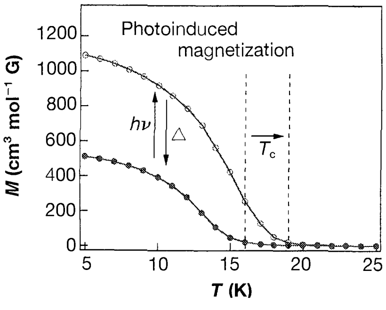

Fig. 3. Field-cooled magnetization versus temperature curves at $H = 5$ G before (●) and after (○) red light irradiation. The magnetization enhanced by illumination (*hν*) can be removed by thermal treatment (Δ) above 150 K.

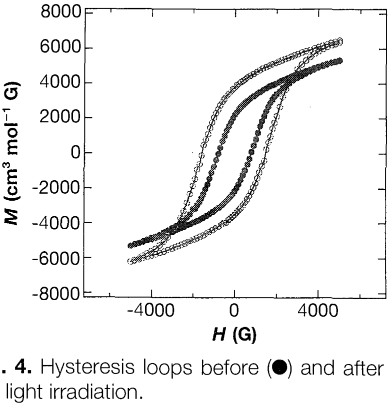

Fig. 4. Hysteresis loops before (●) and after (○) red light irradiation.

By carefully tuning the wavelength of the incident light, the enhancement of the magnetization resulting from red light illumination could be partly negated by blue light irradiation (450 nm with 50-nm half-width, 2.5 mW/cm^2). The magnetization that was decreased with blue light could then be increased again with red light, and the cycle could be repeated (Fig. 5). IR spectra also showed that the CN stretching peak at around 2097 cm^{-1} increased and decreased repeatedly with alternate irradiation with blue and red light.

The change of the magnetization clearly shows that cooperative magnetic phenomena can be influenced by external optical stimuli in a given temperature range. Larger or smaller magnetization enhancement effects could be observed depending on the content of K$^+$. The effect described here is different from conventional light-induced excited spin state trapping (LIESST) (*22, 23*); long-range ordering of spin systems can be controlled for compound 1, whereas LIESST results reported thus far refer to phenomena in the paramagnetic region. The photochemically controllable magnet reported here, as well as the electrochemically controllable one reported previously (*12*), are among the first examples of the phenomenon of tunable magnetism in the field of molecule-based magnets.

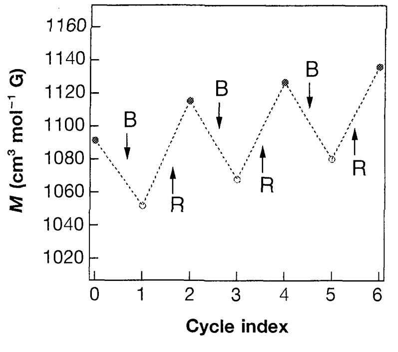

Fig. 5. Magnetization changes induced by alternating blue (B) and red (R) light illumination (10 min) at 5 K. (●) After red light illumination; (○) after blue light illumination.

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18. A 0.5-ml aqueous solution of Co^{II}Cl$_2$ (0.83 mol liter^{-1}) was slowly added to a vigorously stirred 0.5-ml aqueous solution of K$_3$Fe^{III}(CN)$_6$ (0.43 mol liter^{-1}). The resulting precipitate was filtered and washed with methanol and diethylether. The stoichiometry depends on the preparation conditions. When the concentrations of both Co^{II}Cl$_2$ and K$_3$Fe^{III}(CN)$_6$ are increased, the stoichiometric ratio K/Fe tends to increase and the ratio Co/Fe tends to decrease.
19. Elemental analysis of the two compounds [(a) and (b)] obtained under the same preparation conditions (*18*) were as follows: (a) K, 1.74%; Co, 18.50%; Fe, 12.06%; C, 16.97%; N, 18.36%; H, 3.15%; and Cl, 0.3%. (b) K, 2.27%; Co, 18.95%; Fe, 13.00%; C, 17.72%; N, 20.28%; H, 3.38%; and Cl, 0.42%. Computed percentage for K$_{0.2}$Co$_{1.4}$[Fe(CN)$_6$]·6.9H$_2$O: K, 1.83%; Co, 19.34%; Fe, 13.09%; C, 16.89%; N, 19.70%; H, 3.27%; and Cl, 0%.
20. Typical experimental conditions: a powder sample (200 to 300 μg) supported on a commercial transparent adhesive tape was placed on the edge of an optical fiber. Light was shone onto the sample for 5 or 10 min. The magnetization value was then measured after the light was turned off and the temperature reached a steady state. This cycle—illumination and measurement—was repeated.
21. The optical absorption spectrum showed that the absorbance at around 550 nm decreased and the peak at around 400 nm increased due to red light irradiation.
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