Illumination-induced Magnetization Enhancement
of the Weak Ferromagnet [Fe(N$_3$)$_2$(pm)] (pm = Pyrimidine)

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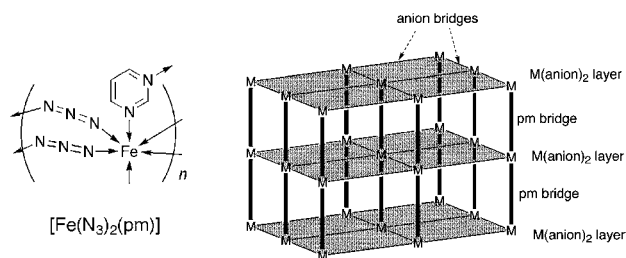[2]*Course of Coherent Optical Science, The University of Electro-Communications, Chofu, Tokyo 182-8585*

The spontaneous magnetization of [Fe(N$_3$)$_2$(pm)] (pm = pyrimidine) was enhanced after UV illumination while the spin-canted antiferromagnetic transition temperature (39 K) was unchanged. Azide-bridged two-dimensional network was damaged on illumination as clarified by IR measurements, possibly leading to an increase of the cant angle.

There have been numerous reports on infinite metal–organic three-dimensional (3D) frameworks which attract much attention for their chemical and physical properties.[1–3] The metal dicyanamides and related mixed-ligand systems characterized as weak ferromagnets (canted antiferromagnets) have intensively studied in the last decade.[4] We and other groups have already reported [M^{II}(L)$_2$(pm)] (pm = pyrimidine; M = Fe and Co for L = N(CN)$_2^-$ and M = Mn and Fe for L = N$_3^-$), which exhibited a pillared-layer structure (Figure 1) and weak ferromagnetism.[3,5,6] These bridging ligands generally play a basic role of antiferromagnetic superexchange couplers.[3,5] The azide ligand is the most versatile ligand in linking transition-metal ions, and actually it has afforded various magnets,[5–9] especially, the pseudo-2D- and 3D-networked weak ferromagnets.[5–8] The origin of the spin canting has been discussed on the basis of the crystal structure and single-ion magnetic anisotropy.[3,10] The μ-1,3 azide bridge has an advantage over μ-1,5 dicyanamide for higher magnetic phase-transition temperatures due to the shorter ion length.[5]

In this letter, we will report observation of the enhanced spontaneous magnetization of [Fe(N$_3$)$_2$(pm)] after UV illumination. The azide group in organic compounds are well known to liberate nitrogen on exposure to light, leaving nitrene as a paramagnetic center.[11] However, such photoreaction of inorganic metal azides have been set aside, partly because of their potentially explosive nature.

The fine crystalline sample of [Fe(N$_3$)$_2$(pm)] was prepared with a great caution and characterized according to the reported method.[5] The sample was stuck on a small piece of a cellophane tape and subjected to magnetic measurements. The precise mass was estimated from the magnetic susceptibility (typically ≈ 0.4 mg). UV light was introduced into a Quantum Design MPMS-7 SQUID probe through a quartz optical fiber (Fujikura large-core fiber S.800/1000; core diameter 800 µm). The light source was a Yamashita Denso Hypercure 200 equipped with a low-pressure Hg lamp (200 W).

The initial magnetic behavior of [Fe(N$_3$)$_2$(pm)] reproduced the reported one.[5] The Fe^{II} high-spin state ($S = 2$) with the $(t_{2g})^4(e_g)^2$ electron configuration was confirmed from the magnitude of the paramagnetic susceptibility. Below 39 K (T_N), the antiferromagnetic phase with spin-canting appeared; the field-cooled magnetization (FCM) showed an upsurge at ≈ 40 K (Figure 2a). After the sample was illuminated in situ with UV light at 5 K for 128 min, the FCM was measured again from 70 K, being remarkably enhanced below T_N, but that of the paramagnetic phase remained practically the same.

The M–H curves of [Fe(N$_3$)$_2$(pm)] (Figure 2b) showed the increase of spontaneous magnetization (M_S) after the UV illumination (210 from 100 erg Oe^{-1} mol^{-1} at 5 K). The strong antiferromagnetic interaction basically retained. The coercive field was also strengthened (13000 Oe from 7000 Oe at 5 K). Since the sample was polycrystalline and the whole specimen could not be subjected to illumination, this behavior showed sample-dependence. However, all of the several runs always exhibited illumination-induced enhancement of FCM by a factor of three

(a)

(b)
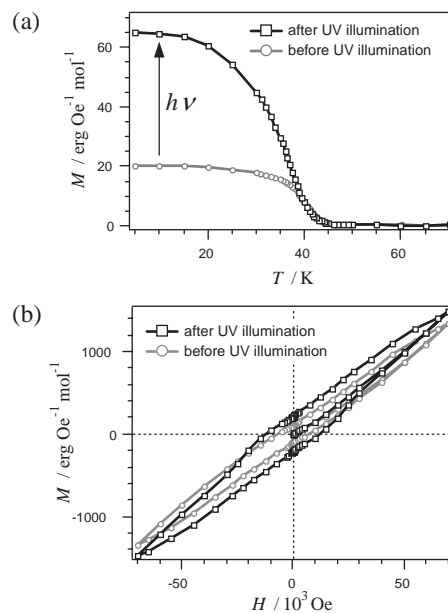
Figure 2. (a) Field-cooled magnetizations at 5 Oe and (b) hysteresis curves at 5 K of [Fe(N$_3$)$_2$(pm)] before and after UV illumination.

anion bridges

[Fe(N$_3$)$_2$(pm)]

Figure 1. Structural formula of [Fe(N$_3$)$_2$(pm)] (left) and a schematic drawing of the pillared-layer structure (right).

to four. Prolonged illumination (>2 h) did not much affect the magnitude of magnetization.

The increase of the magnetization was irreversible. After the sample was annealed at 300 K for a few min or even exposed under ambient conditions, the enhanced magnetization was not lost as clarified by the FCM and hysteresis measurements. No T_N shift was observed. These findings imply that the illumination gave rise to a photoreaction and that the increase of the magnetization did not originate in additional paramagnetic sources such as nitrene. The IR spectrum of the product revealed that the azide stretching band at 2090 cm^{-1} was weakened after the illumination. When a KBr-diluted pellet specimen was illuminated under ambient conditions, 46% was lost after 6 min. The elemental analysis of the product after the illumination indicated a decrease of the nitrogen content.[12] These findings support the photoreaction of the azide group accompanied by a loss of nitrogen.

In sharp contrast to the above results, similar experiments on [Mn(N$_3$)$_2$(pm)] ($T_N = 51$ K)[5] revealed that M_S slightly decreased upon UV illumination.[13] This behavior can be reasonable from a partial decomposition of the 3D structure, leading to a decrease of a molar fraction of ordered manganese ions. Compared with these findings, the anomalous results on [Fe(N$_3$)$_2$(pm)] deserve discussion of the mechanism for the enhancement of M_S.

As the crystallographic analysis revealed,[5] the Fe(N$_3$)$_2$ moiety constructs an infinite and pleated 2D grid parallel to the crystallographic *ac* plane. The pm molecule bridges intersheet Fe ions along the *b* axis to form a trans zigzag Fe–pm chain. The elongated octahedral axes of neighboring Fe ions are inclined each other by 120° owing to the strong directive character of the pm lone pairs. The 2D antiferromagnetic structure on polymeric Fe(N$_3$)$_2$ is rationally explained from the role of an antiferromagnetic coupler of the azide bridge. The pm bridge also works as an antiferromagnetic coupler.[10,14]

The origin of the spin canting has already been discussed for [Fe(N(CN)$_2$)$_2$(pm)].[3] The spin-canting angle is regulated by two competing factors, antiferromagnetic coupling (exchange interaction, $J < 0$) and the axial anisotropy (effective zero-field splitting, $D < 0$) with respect to a pillar direction.[15] The former favors strictly antiparallel alignment whereas the latter leads to spin canting. Assuming that this mechanism holds for [Fe(N$_3$)$_2$(pm)],[16] a possible explanation for the increase of M_S is proposed as follows. The azide-bridged network was damaged, giving rise to weakened J. The contribution of D became relatively larger, and, therefore, the spin-cant angle would be larger. The 3D network structure is tough against partial decomposition of the azide bridge, and consequently the antiferromagnetic transition temperature was hardly changed.

In conclusion, we have clarified the illumination-induced magnetization of [Fe(N$_3$)$_2$(pm)]. Though the spin-canting mechanism is still open to detailed discussion, the results obtained here are important for the development of photoreactive magnetic materials. The irreversible change of magnetization suggests a potential utility of [Fe(N$_3$)$_2$(pm)] as a write-once information-storage medium.

References and Notes

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12 Anal. Initial sample: C, 21.74; N, 49.83; H, 1.69%. A sample after UV illumination for 10 min under ambient conditions: C, 20.44; N, 46.59; H, 1.72%. However, the photoreaction in a SQUID probe took place only to a small extent.

13 The decrease of magnetization suggests that a possible pinning effect due to lattice defects is not a dominant reason for the present photomagnetic properties.

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15 We use the *D* parameter for convenience in discussion, though it is not accurately defined for iron(II) ions.

16 Unfortunately, we could not obtain large single crystals of [Fe(N$_3$)$_2$(pm)] for determination of magnetization anisotropy. However, the spin canting takes place under the conditions where either axial or in-plane anisotropy is operative (i.e., $D < 0$ or $D > 0$), as reported for [Fe(N(CN)$_2$)$_2$(pm)].[3]

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