Magnetophoretic study of photo-induced spin transition of single crystalline particles of cobalt–iron Prussian blue analogues

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Abstract

The photo-induced spin transition of crystalline microparticle of Co–Fe Prussian blue analog was investigated by means of magnetophoresis. An apparatus to observe the photo-induced spin transition of a single microcrystal in suspension was constructed, and the magnetophoretic velocities before and after the irradiation with 532 nm pulse laser were observed. The photo-induced spin transition from a low-spin state to a high-spin state of the microparticle was observed from the abrupt increase of the magnetophoretic velocity after the irradiation. The threshold value for spin transition was estimated to be lower than 10 mJ cm$^{-2}$ by this method, more precisely than that reported from SQUID magnetometer measurements. Moreover, the magnetic susceptibility of an individual particle after irradiation was calculated from the magnetophoretic velocity change. The magnetic susceptibility values determined by the present method were highly scattered. This was caused not only by the experimental error resulting from Brownian motion but also by the difference in the spin transition probability for individual particles. The effect of size on the spin transition phenomena was discussed.

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1. Introduction

There are a number of separation and characterization methods for molecules and ions, including high performance liquid chromatography, capillary electrophoresis, and solvent extraction. On the other hand, separation and characterization methods for micrometer-sized particles in liquids are still rather limited [1]. Innovative principles for the migration of microparticles like colloids, DNAs, and cell composites are highly required. Migration analysis employing external fields has a potential to satisfy that demand. In particular, magnetophoresis has been utilized to separate microparticles according to their magnetic properties [2–4]. One of the specific properties of magnetic field, $H$, different from electric field is that there is no magnetic monopole, that is $\text{div}H=0$, which causes the difficulty of shielding. This seems to be disadvantage. However, in the case of separation of microparticles, this feature can become an advantage; Almost all materials are permeable to magnetic fields, which can thus cause particle migration without contact. Another advantage of magnetophoresis is that every substance has its own magnetic property. For example, the magnetism of transition metal complexes, which is governed by the valence number and the spin state induced by ligand or crystal field, can be observed for individual microparticles.

In the field of modern material sciences, molecule-based magnetic materials have been extensively studied, because the design of their properties is easier compared to that of classical magnetic materials such as metal alloys and metal oxide [5,6]. In particular, Prussian blue analogues show various characteristic magnetic properties depending on their transition metal ion [7–10]. A phenomenon of special interest is photo-induced spin transition [11]. This was discovered in Co–Fe Prussian blue analogues. This material has bistable spin state in a certain temperature region depending on the composition and the valence state of metal ions. In a characteristic temperature region, this material exhibits spin transition by photo irradiation, thus the magnetic susceptibility is changable by light.

We have developed a novel technique called ‘magnetophoretic velocimetry’. This technique can measure not only the volume magnetic susceptibility of a migrating particle, but also the amount of paramagnetic ions including in and adsorbing on the microparticle, from the magnetophoretic velocity under an...
inhomogeneous magnetic field [12]. Recently, we demonstrated that photo-induced spin transition of Co–Fe Prussian blue analog could be detected by magnetophoresis [13]. The purpose of this study is to show a new applicability of magnetophoresis as an analytical technique of photo-induced spin transition.

2. Experimental section

2.1. Synthesis of Co–Fe Prussian blue analogues

Co–Fe Prussian blue analogues were prepared by a solution reaction of K$_3$[Fe(CN)$_6$] (Wako Pure Chemical Industries Ltd, Osaka, Japan) and CoCl$_2$ (Nacalai Tesque, Inc., Kyoto, Japan), controlling the NaCl concentration and adjusting the reaction temperature by a water bath. A Co–Fe polycyanide precipitate was produced soon after the addition of an aqueous solution of K$_3$[Fe(CN)$_6$] (2 mM) and NaCl (5 M) to an aqueous solution of CoCl$_2$ (2 mM) and NaCl (5 mM) at 50°C. The precipitate was filtrated, washed by water and dried. A scanning electron microscope (JEOL, Tokyo, Japan) image shown in Fig. 1(a) confirmed that a 1–2 µm sized cubic crystalline powder sample was produced. One milligram of the powder was dispersed in 3 mL water by sonication, and this was used as a sample suspension.

Water was purified by milli-Q system (Millipore, Bedford, UK) and the other reagents were used as received.

2.2. Experimental setup

Fig. 2 illustrates the laser-induced magnetophoresis apparatus used in this study. The square fused-silica capillary with 100×100 µm inner section (Polymicro Technologies, Phoenix, USA) was used as a cell for the magnetophoresis. The sample solution was introduced into the cell by utilizing the capillary rize. An inhomogeneous magnetic field was generated by a pair of iron pole pieces and Nd–Fe–B permanent magnets (Mas Material, Tokyo, Japan) [14]. The surface magnetic flux density of this permanent magnet was 0.4 T. The second harmonic light (532 nm) of a pulsed Nd:YAG Laser (Continum, Surelite I-10, CA, USA) was irradiated into the focal plane of the microscopic system via a slit, a tube lens (Mitsutoyo, MT-1, Kanagawa, Japan), and an objective (Mitsutoyo, MPlan NUV 50×, Kanagawa, Japan). The pulse width were 5–7 ns. The energy density at the focal plane was controlled from 5 to 40 mJ cm$^{-2}$ per pulse with the neutral density (ND) filter and adjusting the delay time of Q-switch from flash lamp of laser. The irradiation area was set to 50×50 µm by adjusting the mask. The magnetophoretic behavior near the edge of the pole pieces was observed by CCD camera (ELMO, CN42H, Nagoya, Japan), and the magnetophoretic velocities were obtained from the captured images. All measurements were carried out in a thermostated room at 25 ± 1°C.

3. Results and discussion

3.1. Magnetophoretic behavior of Co–Fe Prussian blue micro crystalline particle before and after photo induced spin transition

Shimamoto et al. demonstrated the interesting photo-magnetic properties of Co–Fe Prussian blue analogues [15]. According to their report, Co–Fe Prussian blue analogues had a face-centered cubic structure composed of Fe, Co and CN as shown Fig. 1(b). At low temperature, the spin states of both Co and Fe were low spin state ($t^6 g^0 e^0 S=0$), called low temperature phase (LT phase). When the LT phase was heated, an electron of Fe(II) transferred to Co(III), producing the high

![Fig. 1. SEM image (a) and the structure (b) of Co–Fe Prussian blue analog.](image)

![Fig. 2. Experimental setup for the observation of the photo-induced spin transition during the magnetophoretic migration of a single particle.](image)
spin state Co(II), because the Co–N bond length was increased and hence the crystal field was weakened and the reducing power of Co became smaller. As a result, in the high temperature (HT) phase, the spin states of Co and Fe became $t^5_2 e^2_g$ ($S = 3/2$) and $t^5_2 e^0_g$ ($S = 1/2$), respectively. This thermal process was reversible, although the transition had a hysteresis loop; the transition temperature in the cooling process was lower than that in the heating process. The transition temperature region in the hysteresis loop was dependent on the composition of Co and Fe. Moreover, they reported that Co–Fe Prussian blue analogues exhibited bistability between HT phase and LT phase, and one-shot pulse laser of 532 nm could induce the phase transition from LT to HT phase at the temperature in the hysteresis loop region. The compound synthesized in this study had a bistability and exhibited photo-induced spin transition at the room temperature [16]. Typical magnetophoretic behavior of a single crystalline particle was shown in Fig. 3. This image was made by superimposing microphotographs observed at 0.1 s intervals. The crystalline particle was attracted into the gap of the pole pieces by the magnetic force, and the magnetophoretic velocity was suddenly increased after the irradiation of a single shot of pulse laser. The velocity jump is attributable to the change of the magnetic susceptibility generated by the photo-induced spin transition [14]. The $x$-components of the magnetophoretic velocities of the particles were plotted against time as shown in Fig. 4. The $x$-direction was defined as that directed into the gap of the pole pieces along the capillary and $x=0$ was set at the edge of the pole pieces as indicated in Fig. 3. The magnetophoretic velocity was changed within at least 1/30 s.

3.2. Pulse energy threshold for photo-induced spin transition

The magnetophoretic velocity jump was observed with changing the pulse energy. Fig. 5 shows the fraction of the number of particles, whose velocity increased more than 1.5 times after irradiation, to all observed particles, which was plotted against energy density of the laser pulse. The photo-induced magnetophoretic velocity jump was not observed in lower pulse energy than 5 mJ cm$^{-2}$, while about 85% of the particle exhibited the acceleration at energy above 20 mJ cm$^{-2}$. However, this means the 15% of all particle did not exhibit spin transition. This kind of behavior of this compound has been already reported [16], however, the reported threshold value was 64 mJ cm$^{-2}$. Hence, the reported value was about three times larger than the present value. This is attributable to the difference of the measurement system. In the report [16], the magnetic susceptibility change of the powder sample was measured in situ by a SQUID magnetometer, where the pulse laser could not irradiate the entire sample enough to cause the spin transition of all crystals.

The photo-induced acceleration in the magnetophoretic velocity of the crystalline microparticle was analysed by the general principle of magnetophoresis. The $x$-component of magnetophoretic velocity, $v_m$, in a liquid medium can be

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Fig. 3. Typical magnetophoretic behaviors of Co–Fe Prussian blue analogue. This microphotograph was made by superimposing images at 0.1-s intervals. The dashed line illustrates the edge of pole pieces, and the black arrows indicate the irradiated position of pulse laser for crystalline microparticles.

Fig. 4. Magnetophoretic velocities vs. time. The arrow shows the pulse laser irradiated point.

Fig. 5. The fraction of the number of particles exhibiting the photo-induced magnetophoretic acceleration to all observed particle (253 particles). The solid line is an eye guide.
expressed as follows

\[ v_m = \frac{(x_p - x_m)}{\mu_0 \eta} \frac{V}{f} B \frac{dB}{dx} \]  

(1)

where \( x_p \) and \( x_m \) are the magnetic susceptibilities of a particle and a medium, respectively, \( V \) the volume of a particle, \( \mu_0 \) vacuum magnetic permeability, \( \eta \) the viscosity of a medium, \( f \) the friction coefficient of the drag force, and \( B \) the magnetic flux density. In a very low Reynolds number fluid (<0.05), the coefficient of the drag force of an isometric particle, e.g. sphere, cube, octahedron, or tetrahedron, can be approximated as an equivalent volume sphere by utilizing the following coefficient of drag force [17]

\[ f = 6\pi \eta r_s/K \]  

(2)

where

\[ K = 0.843 \log_{10} \frac{\psi}{0.065} \]  

(3)

and \( r_s \) is the Stokes radius, that is, the radius of the sphere having the same volume as the isometric particle. The sphericity, \( \psi \), is defined as follows

\[ \psi = A_A/A \]  

(4)

where \( A_A \) and \( A \) are the surface area of a particle and the sphere having the same volume as the particle. \( K \) is equal to 0.922 for a cubic particle by using the sphericity, \( \psi = 0.806 \). In the present system, Reynolds number was smaller than 10^{-4}, therefore, the Stokes regime was applicable.

\( B(dB/dx) \) in Eq. (1) is the function of a position, however, \( B(dB/dx) \) was found to be actually constant (1800 T/m) in the observation region. Therefore, the increase in the ratio of the magnetophoretic velocity after the irradiation of pulse laser can be evaluated by the equation

\[ \frac{v_a}{v_b} = (x_{p,a} - x_m)/(x_{p,b} - x_m) \]  

(5)

where the subscripts a and b represent after and before the irradiation, respectively. Therefore, the velocity ratio can be rewritten as the ratio of the magnetic susceptibility before and after the irradiation. The mean of the velocity ratio was 2.8 ± 1.4 for 10^2 particles where the irradiation pulse energy was larger than 18 mJ cm^{-2} pulse^{-1}. This was slightly higher than the value of 2.4, which was measured by SQUID magnetometer for a macro-sample [16], and the observed velocity ratio seems to have a somewhat large variability. It could be considered that the reason for these results might be ascribed to the size of the particle, because the size was not regarded in the discussion of the velocity ratio unless this ratio should relate with the volume magnetic susceptibility as indicated in Eq. (5).

### 3.3. The size estimation of the individual particles

Unfortunately, the clear images for the size determination of a single particle could not be obtained due to the limited resolution of the optical microscope, whose resolving power was 0.7 \( \mu \)m for illumination light of 550 nm, and the chromatic aberration caused from the high numerical aperture of the objective and the square capillary. Accordingly, the Stokes radius, \( r_s \), was calculated from the magnetophoretic velocity by using the derived form from Eq. (1). Substitution of Eq. (2) into Eq. (1) yields:

\[ r_s = \left( \frac{9}{2} \frac{\mu_0 \eta v}{(x_p - x_m)K} \left( \frac{B}{dB/dx} \right)^{1/2} \right) \]  

(6)

We assumed three ‘ideal’ cases to obtain \( r_s \) from the magnetophoretic velocity: (A) The spin state before irradiation is homogeneous throughout all particles, but there are differences between the particles after the irradiation, i.e. the values of \( x_{p,b} \) of all particles are constant while those of \( x_{p,a} \) are scattered. (B) The contrary case of (A), that is, the spin states after irradiation are constant (\( x_{p,a} = \) constant), however, those before the irradiation are different from each particle \( (x_{p,b} = \) scattered). (C) The concentrations of the atoms concerning the spin transition are same in any particles. Hence, the differences between \( x_{p,a} \) and \( x_{p,b} \) are always constant. In order to decide the most plausible model among above three cases, we calculated the average magnetic susceptibility. For example, in the case of (A), \( r_s \) was obtained from \( v_b \) and the reference value of \( x_{p,b} \), and then the average value of \( x_{p,a} \) was calculated by substituting the value of \( r_s \) and observed \( v_a \) into Eq. (1) for each particle. The average value of the magnetic susceptibility, \( \chi_{ave} \), was estimated by using following equation that took account of the volume of individual particles, \( V_i \)

\[ \chi_{ave} = \frac{\sum_i \chi_i V_i}{\sum_i V_i} \]  

(7)

where \( \chi_i \) is the volume magnetic susceptibility of the individual particle. The results of this calculation is listed in Table 1. In the case of the assumption (A), the magnetic susceptibilities of observed and reference data were in good agreement with each other. Therefore, it was suggested that the spin state before the irradiation did not vary for individual particles, and, in the following discussion, we used the \( r_s \) value calculated from \( v_b \) for individual particles.

### 3.4. Examination for individual particles

We investigated the magnetophoretic velocity before and after the pulse irradiation for individual particles in order to clarify the meaning of the large fluctuation of \( v_a/v_b \) values. First, the dependence of the ease of the spin transition on the size of particle was examined. Fig. 6 shows the distribution of observed particle radii (hatched bar) and the histogram of the converted particle (white bar) size among all observed particles.
at (a) 10.1, (b) 16.1, (c) 18.3, and (d) 22.7 and 33.7 mJ cm\(^{-2}\) per pulse for the laser pulse energies. It is reasonable to consider that the distribution of the size did not change in each histograms. The white bars show the number of events that showed the spin-transition. By irradiation of weaker light of 10.1 mJ cm\(^{-2}\) per pulse (Fig. 6(a)), the relatively smaller particles were converted. This means that the spin state of the smaller particle could be more easily photo-converted. Using stronger irradiation energy (\(< 15\) mJ cm\(^{-2}\) pulse\(^{-1}\)), no significant dependence of size on the conversion fraction was observed (Fig. 6(b)–(d)).

Fig. 7 shows the plot of the velocity after the irradiation against \(r_s\), in which \(v_a\) depended on \(r_s\) quadratically as predicted by Eq. (6). The solid line indicates the calculated velocity from the reference data \((\chi_{p,a} = 174.7 \times 10^{-6})\). The dotted line was obtained by using the least square method for all observed data.

Two lines were in good agreement with each other, although the individual experimental values of \(v_a\) were scattered. The volume magnetic susceptibility of the individual particle, \(\chi_{p,a}\), was plotted against \(r_s\) in Fig. 8. \(\chi_{p,a}\) of the smaller particles were highly scattered and sometimes much higher than the reference data as mentioned above, indicated by the solid straight line (a) the dashed line (b) shows the literature value of \(\chi_{p,b}\). There was no particle, which has \(\chi_{p,a}\) lower than \(\chi_{p,b}\). The dotted line (c) represents the calculated value of the magnetic susceptibility, \(\chi_{p,c}(249 \times 10^{-6})\), provided that all cobalt atoms are converted to high spin state. Some scattered observed values were larger than even \(\chi_{p,c}\).

As the origin of the scattering, the contribution of Brownian motion, which is an inherent phenomenon for small particles in liquid, was considered. The mean displacement of the small particle can be expressed by using the Boltzman constant, \(k_B\),

![Fig. 6. The histograms of the size distribution of all observed particle (hatched bar + white bar) and of those particles that exhibit the magnetophoretic velocity change (white bar). The irradiated pulse energy densities were 10.1 (a), 16.1 (b) and 18.3 (c), and 22.7 and 33.7 mJ cm\(^{-2}\) pulse\(^{-1}\) (d). The numbers of observed particles were 53 (a), 65 (b), 55 (c), and 50 (d).](image)

![Fig. 7. The velocity after pulse laser irradiation plotted against \(r_s\); the solid line indicates the calculated value by using the reference data measured by SQUID magnetometer [16]. The dotted line was obtained by the least square method.](image)

![Fig. 8. \(\chi_{p,a}\) of individual particles as a function of \(r_s\). The solid (a), dashed (b), and dotted straight line (c) indicate the value of \(\chi_{p,a,ave}\), \(\chi_{p,b}\), and \(\chi_{p,c}\) respectively. The curves represents the deviation value attributable to Brownian motion if the particle, which has \(\chi_{p,a}\) (a), \(\chi_{p,b}\) (b) and \(\chi_{p,c}\) (c) of the magnetic susceptibility.](image)
and the temperature, $T$, as follows

$$\langle |x| \rangle = \sqrt{\frac{2k_B T}{f}}$$  \hspace{1cm} (8)

where $t$ is time. Then, the fluctuation of the velocity during the velocity measuring time, $t_{\text{mes}}$, can be derived from Eqs. (2) and (8):

$$\Delta v = \langle |x| \rangle / t_{\text{mes}} = \sqrt{\frac{K k_B T}{3\pi \eta r t_{\text{mes}}}}.$$  \hspace{1cm} (9)

The measuring time was 0.5 s. This was treated as the error affecting the spread of $\chi_{p,a}$. Then, the error attributed to Brownian motion can be written as

$$\Delta \chi_{p,a} = \frac{A_1}{A_2} \left[ \frac{1}{2} \left( \frac{1}{\chi_{p,b} - \chi_m} \right)^2 + \left( \frac{1}{\chi_{p,a} - \chi_m} \right)^2 \right]^{1/2} \chi_{p,a} r_s^{-5/2}.$$  \hspace{1cm} (10)

where

$$A_1 = \sqrt{\frac{K k_B T}{3\pi \eta t_{\text{mes}}}}.$$  \hspace{1cm} (11)

and

$$A_2 = \frac{2}{9 \kappa_B T} \left( \frac{d B}{d x} \right).$$  \hspace{1cm} (12)

$(\chi_{p,a} \pm \Delta \chi_{p,a})$ was calculated for $\chi_{p,a} (= \chi_{p,a,\text{ave}})$, $\chi_{p,b}$, and $\chi_{p,c}$. $\chi_{p,a}$ as a function of $r_s$, as shown in Fig. 8 by the solid, dashed and dotted curves, respectively. These curves means that $\chi_{p,a}$ can be scattered between the two lines, i.e. $(\chi_{p,a} - \Delta \chi_{p,a})$ and $(\chi_{p,a} + \Delta \chi_{p,a})$ due to Brownian motion. It should be noted that (1) the maximum value of $\chi_{p,a}$ for any $r_s$ is almost the same, if the probability to convert more Co(III) to Co(II), and the fact (2) implies that almost all Co(III) could be converted to the high spin state by only one-shot pulse laser in some particles. However, this does not mean that the many pulses can convert the surface domains more easily than the larger ones are required. The difference caused by the size of the particle is the specific surface area. Therefore, it is thought that the domain on the surface is easily converted, and then the magnetophoretic velocity of the small particle, which had large specific surface area, could be changed by lower pulse energy. In Fig. 8, the value of $\chi_{a}$ increased with the decrease of the size. From these results, it is suggested that the spin transition of the surface domains easily occurs in comparison with the inside bulk domains.

4. Conclusion

We observed the magnetophoretic behavior of microcrystalline particles of a Co–Fe Prussian blue analogue, which exhibits photo-induced spin transition at room temperature, before and after the pulse laser irradiation. The spin transition could be observed as an increase of the magnetophoretic velocity.
The value of the threshold energy density of pulse laser observed in this work was smaller than a literature value measured by SQUID magnetometer, because the presented system allowed us to irradiate single particles and there was no loss of the pulse energy by scattering or absorbing by other particles. This is one of the advantages to treat a single particle.

The magnetic susceptibility after irradiation could be measured, but the experimental data were scattered. The reason for this scattering was considered as the spread of velocities caused by Brownian motion. However, even taking into account Brownian motion, the $\chi_{p,a}$ value of some particles were much higher than the average and attained the calculated value assuming the case that all Co atoms were converted to high spin state. Therefore, it was suggested that the surface domain more readily exhibits the spin transition and the value of the magnetic susceptibility of the surface is higher than that of the inside domain.

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