Size dependence of the photoinduced magnetism and long-range ordering in Prussian blue analogue nanoparticles of rubidium cobalt hexacyanoferrate

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\textbf{Abstract.} Nanoparticles of rubidium cobalt hexacyanoferrate (Rb\textsubscript{x}Co\textsubscript{y}[Fe(CN)\textsubscript{6}]\textsubscript{z} \cdot nH\textsubscript{2}O) were synthesized using different concentrations of polyvinylpyrrolidone (PVP) to produce four different batches of particles with characteristic diameters ranging from 3 to 13 nm. Upon illumination with white light at 5 K, the magnetization of these particles increases. The long-range ferrimagnetic ordering temperatures and the coercive fields evolve with nanoparticle size. At 2 K, particles with diameters less than approximately 10 nm provide a Curie-like magnetic signal.
1. Introduction

The investigation of magnetism in the molecule-based solid Prussian blue, Fe₄[Fe(CN)₆]₃ · xH₂O, and related analogues has a rich history [1, 2], dating back to 1928 [3]. Measurements down to liquid helium temperatures identified the transition to long-range ferromagnetic order [4]–[6], but an understanding of the magnetic interactions remained elusive until the 1970s, when x-ray [7] and neutron [8] diffraction data identified the crystal structure and the spin delocalization from high-spin Fe(III) to low-spin Fe(II). Interest in these materials was renewed in the 1990s with the synthesis of several mixed-metal Prussian blue analogues with higher magnetic ordering temperatures, along with the 1996 discovery of long-lived photoinduced magnetism in K₀.2Co₁.4[Fe(CN)₆] · 6.9H₂O [9]. A flurry of experimental and theoretical research has elucidated the fundamental nature of the light-induced effects in three-dimensional bulk materials [10, 11], and recent efforts have been made to integrate the photoinduced magnetism into films [12]–[18] and nanoparticles, which have technical and biophysical applications. There have been several efforts to synthesize nanoparticles of Prussian blue analogues [19]–[31], but only a few examples of photoinduced magnetism in these particles have been reported,³ including work that isolated K₀.5Co₀.5[Fe(CN)₆] · nH₂O particles with typical diameters of 8–10 nm within a silica xerogel [22] and other research producing 11 nm × 70 nm nanorods of Mo(CN)₈Cu₂ protected by polyvinylpyrrolidone (PVP) [26]. In each case, although photoinduced magnetism was observed, the particles did not exhibit long-range order.

The purpose of this paper is to report our ability to synthesize Rb₀.5Co₀.5[Fe(CN)₆] · nH₂O nanoparticles protected by PVP that exhibit photoinduced magnetism for all sizes and that possess long-range ordering, with coercive fields ranging between 0.25 and 1.5 kG, in the larger particles. The magnetic properties evolve with size, where at 2 K, the particles with diameters less than approximately 10 nm provide a Curie-like magnetic signal.

³ Here, we differentiate photoinduced magnetism, which is used to describe the intrinsic process of the A₀.5Co₀.5[Fe(CN)₆] · nH₂O Prussian blue analogue, from photoswitchable magnetism, which arises from magnetization changes observed upon photoexciting a functionalized component or coating of Prussian blue analogue nanoparticles [29, 30].
Table 1. A summary of the materials properties of the four sets of samples.

| Batch | Starting PVP (g) | Resulting chemical formula | PVP:Co ratio | Diameter (nm) | T_{C, onset} (K) | T_{C, onset} (K) | H_{C, onset} (G) | H_{C, onset} (G) |
|-------|-----------------|-----------------------------|--------------|---------------|-----------------|-----------------|-----------------|-----------------|
| A     | 1.0             | Rb_{1.9}Co_{4}[Fe(CN)_{6}]_{3.2} · 4.8H_{2}O | 360          | 3.3 ± 0.8     | < 2             | < 2             | < 10            | < 10            |
| B     | 0.5             | Rb_{1.8}Co_{4}[Fe(CN)_{6}]_{3.2} · 4.8H_{2}O | 200          | 6.9 ± 2.5     | 10              | 13              | ~ 15            | ~ 30            |
| C     | 0.2             | Rb_{1.7}Co_{4}[Fe(CN)_{6}]_{3.2} · 4.8H_{2}O | 60           | 9.7 ± 2.1     | 13              | 17              | 250             | 330             |
| D     | 0.1             | Rb_{0.9}Co_{4}[Fe(CN)_{6}]_{2.9} · 6.6H_{2}O | 20           | 13.0 ± 3.2    | 19              | 22              | 1000            | 1500            |

2. Synthesis and characterization

Our Rb_{j}Co_{k}[Fe(CN)_{6}] \cdot nH_{2}O nanoparticles were synthesized by modifying the procedure for Prussian blue nanoparticles described by Uemura and co-workers [23, 24]. A 2 mL solution containing both 28 mg K_{3}Fe(CN)_{6} (0.085 mM) and 6.8 mg RbNO_{3} (0.046 mM) was added dropwise to an 8 mL solution containing 30 mg Co(NO_{3})_{2} · 6H_{2}O (0.103 mM) and PVP while stirring rapidly. By varying the amount of PVP (table 1), the protocol produced samples with different particle sizes and size distributions. After 30 min of stirring, the solution was allowed to sit for one week. For transmission electron microscopy (TEM) studies, a 50 \mu L aliquot of the suspension was diluted 2000 times, and 8 \mu L of the diluted suspension was placed on a holey carbon grid. A representative image is shown in figure 1, and selected area electron diffraction was compared to powder x-ray diffraction patterns to confirm the structure [32]. In addition, infrared spectra displayed a C–N stretch of 2124 cm^{-1}, consistent with a Co(III)–Fe(II) low-spin pair. Using Image J imaging software [33], the TEM images were analysed to obtain the particle size distributions shown in figure 2. These data were fit to a log-normal function that yielded the characteristic diameters shown in figure 2 and table 1. To isolate the particles, three volumes of acetone were added to the synthesis solution, which was centrifuged, and then further washed with acetone and dried under vacuum. Chemical analysis was obtained from a combination of CHN combustion analysis and inductively coupled plasma mass spectrometry (ICP-MS), and the resulting formulae are listed in table 1, along with the ratio of the PVP repeat unit per cobalt. The extent of H_{2}O coordination to Co was estimated by considering the Fe vacancies implicit with the measured Co:Fe ratio.

3. Photoinduced magnetism

The temperature dependences of the dc magnetic susceptibilities, \chi(T) = M/H, of the four batches of particles are shown in figure 3. A standard commercial SQUID magnetometer was employed, and the samples were mounted to commercial transparent tape and could be irradiated with light from a room temperature, halogen source by using a home-made probe equipped with a bundle of optical fibres [17]. Small diamagnetic background contributions from the holder and tape (representing \lesssim 0.1% of the total signal) were independently measured and have been subtracted from the data. The magnetic signals are expressed per mole of sample using the

4. Energy dispersive spectroscopy (EDS) on similar samples suggests the possibility of trace amounts of K, from the K_{3}Fe(CN)_{6} solution, being incorporated as interstitials.

5. Similar size distributions have been obtained for Prussian blue nanoparticles protected by PVP [28].
Figure 1. TEM image of a collection of Rb$_{0.9}$Co$_{0.1}$[Fe(CN)$_6$]$_{2.9}$·(H$_2$O)$_{6.6}$ nanoparticles from batch D, see table 1.

chemical formula listed in table 1. The dark state zero-field cooled (ZFC) data were obtained after cooling in zero applied field from 300 K, while the dark state field-cooled (FC) data were taken after cooling in 100 G from 300 K. The light state was established after field cooling the samples from 300 to 5 K in 100 G and subsequently irradiating with light for 5 hours, which saturated the photoinduced response. In order to avoid spin glass-like relaxation, the light state FC data were obtained after cycling the sample to 30 K in 100 G.

4. Discussion

It is noteworthy to recall that the photoinduced magnetism of the Prussian blue analogues depends upon a charge transfer-induced spin transition (CTIST) event, requiring the presence of vacancies to allow crystalline flexibility [34]–[41]. More specifically for Rb$_j$Co$_k$[Fe(CN)$_6$]$_l$·nH$_2$O, the spins of an Co–Fe pair can exist in either of two arrangements. The low-spin state consists of Co(III) (S = 0) and Fe(II) (S = 0), while the high-spin state possesses Co(II) (S = 3/2) and Fe(III) (S = 1/2). The presence of the CTIST effect depends on the local chemical environment defined by the values of $j$, $k$, $l$ and $n$ in the chemical formula. For limiting ratios, Co and Fe spins can be locked into either their high-spin or low-spin states for all accessible temperatures. Alternatively, with the proper tuning of the chemical ratios, the Co and Fe ions can exist in high-spin states at room temperature and then experience a crossover to their low-spin states at approximately 150 K. The spin crossover phenomenon generates the pairs involved in the photoinduced magnetism. However, since the CTIST effect may not be 100% efficient, some regions remain locked in their high-spin states, and we refer to them as primordial spins [13].
For example, these primordial spins are responsible for the magnetic signals observed for the dark state of the largest particles. When irradiated, the low-spin regions, near the primordial high-spin clusters, are photoinduced to the high-spin magnetic state, resulting in a growth of the magnetic domain. This scenario is supported by our description of the anisotropic photoinduced magnetism observed in thin films [13, 18] and by the local probe investigations of others [42, 43]. All samples show a photoinduced increase in their magnetic signals, and the strength of the change...
Figure 3. The temperature dependences of the low field, 100 G, susceptibilities are shown for the ZFC dark (♦), FC dark (■), and FC light (□) states of each batch produced. The insets display the differences between the FC light and dark states, as described in the text. Finite values for this difference can only arise from photoinduced magnetism.

is correlated with the size of the particles. The differences between the FC susceptibilities of the light and dark states,

\[ \Delta \chi = \chi_{\text{FC}}^{\text{light}} - \chi_{\text{FC}}^{\text{dark}}, \]

are plotted in the insets of figure 3, and finite values can only arise from the photoinduced magnetism. It is important to stress that photoinduced magnetism is observed even in small particles possessing only Curie-like behaviour.

Two main features are seen when considering the evolution of material properties due to the increasing average size of the separate batches, namely the onset of long-range magnetic order and an increasing net magnetization. This scaling of magnetization is linked to an increased diamagnetic-surface to magnetically-active-volume ratio at smaller particle sizes. At low temperatures, the high-spin Co and Fe ions interact antiferromagnetically, giving rise to a ferrimagnetic transition at \( T_C \), which is about 24 K for bulk powder specimens with a similar
Figure 4. The dark state, i.e. primordial, ZFC (♦) and FC (■) states show a signal associated with long-range order for the two batches displaying a mix of magnetic behaviour after subtracting the Curie-like contribution. The susceptibility of batch A only exhibits a Curie-like contribution, while the magnetic signal for batch D is dominated by spins that are ordered, see text for details. For each sample, a Curie-like contribution was obtained by fitting the dark state data above 30 K, and this magnetic signal was subtracted from the FC and ZFC dark state data shown in figure 3.

chemical formula [36]. For the magnetic data shown in figure 3, the onset of this transition can be estimated, and these macroscopic temperatures are listed in table 1. We contend that particles larger than a critical size will allow domains large enough to approach bulk-like magnetic properties. Conversely, smaller particles may put limits on allowed domain size, suppressing the ordering temperature. Microscopically, if the size of the magnetic domains is less than or of the order of the magnetic coherence length, then a spectrum of $T_C$ values can be expected, and evidence of this trend is observed in batches C and D, see the insets of figure 3. In other words, the size distributions may include particles both above and below the critical size that leads to bulk-like properties. As a result, the magnetic response of each batch may include contributions from Curie-like and bulk-like fractions. The percentage of each can be estimated by subtracting a Curie-like signal from each $\chi(T)$ plot, and the results for batches B and C are shown in figure 4.

In contrast, batch A follows Curie-like behaviour, whereas the active sites in batch D are almost entirely ferrimagnetically ordered. This analysis of the data suggests the Curie-like contribution for each of the four batches of nanoparticles (smallest to largest) is 100, 90, 50 and 10%. Consequently, at least down to 2 K, nanoparticles with sizes below $\sim$10 nm do not exhibit long-range order. These interpretations are consistent with our $M$ versus $H$ measurements performed at 2 K, where coercive fields, $H_C$, and remnant magnetization values are observed for the largest sets of particles but not for the smallest set of particles, figure 5 and table 1. Furthermore, the differences between the FC and ZFC data for the dark states in batches B, C and D are consistent with spin glass or cluster glass behaviour [44, 45], and our ac susceptibility data are presented in the appendix.

Independently, we have generated bulk samples with light state $T_C$(onset) $\approx$ 24 K.

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Figure 5. The $T = 2$ K magnetization versus magnetic field sweeps for the two largest sizes of nanoparticles, batches C and D, are shown for the light (○ and □) and dark (● and ■) states. The coercive fields, $H_C$ for the light and dark states for each batch are listed in table 1, and the lines are guides for the eyes.

5. Conclusions

In conclusion, we have synthesized four different sizes of Rb$_2$Co$_4$[Fe( CN)$_6$]$_3$·n H$_2$O nanoparticles protected by PVP. Each batch of particles exhibits photoinduced magnetism, but the strength of this effect, as well as other global properties, e.g. $T_C$ and $H_C$, are correlated with the intrinsic particle size distributions of each batch. The combination of photoinduced magnetism and nanosized Prussian blue analogue particles with finite coercive fields is unique and establishes a length scale limit of $\sim 10$ nm for these properties. The next advances in the field will undoubtedly employ Prussian blue analogues with higher transition temperatures [46] that may have a variety of technical applications, including, for example, the exploitation of optically controlled magnetocaloric properties [47].

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Figure A.1. The temperature dependences of the real ($\chi'$) and imaginary ($\chi''$) ac susceptibilities of the ZFC dark states, i.e. primordial states, are shown for all four batches of nanoparticles. All batches were measured with no applied static field and an alternating field of 4 G, except for batch D, which was measured in 1 G. The frequency dependence was studied at 1 Hz (●), 10 Hz (●), 100 Hz (○), and 1 kHz (▲) for all batches, except for batch D, which has an additional measurement at 333 Hz (★). Arrows are guides for the eyes and pass through the peaks.

Appendix

The temperature dependences of the real ($\chi'$) and imaginary ($\chi''$) ac susceptibilities of the ZFC dark states, i.e. primordial states, of all four batches are shown in figure A.1. The phenomenological parameter, $\beta$, given by [44]

$$\beta = \frac{\Delta T_f}{T_f \Delta (\log \omega)}$$  \hspace{1cm} (A.1)

where $T_f$ is the freezing temperature given by the cusp in $\chi'(T)$ and $\omega$ is the angular frequency, is $0.024 \pm 0.004$ for batches C and D, and this observation is consistent with spin glass or cluster glass behaviour [44, 45].
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