Photoenhanced Ferromagnetism in High-K⁺-Containing K–Ni–Cr Prussian Blue Analogues Coated on Rb–Co–Fe Nanocubes

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ABSTRACT: A large enhancement of the Ni and Cr ferromagnetic moments under UV-light irradiation has been detected in 55 nm thick K₀.₉₈NiᵢCr(CN)₆₋₀.₇₀(H₂O)₀.₃₀·₀.₁₁H₂O Prussian blue analogues coated on 240 nm Rb₀.₇₆CoᵢFe(CN)₆₋₀.₇₄(H₂O)₀.₂₆·₀.₅₆H₂O nanocubes. Two separate magnetic transitions were found. The one at 72 K marks the magnetic ordering of the Ni and Cr ions on the shell. A higher degree of electronic connection along the Ni–N–C–Cr–N–Ni chains was achieved by the incorporation of a larger amount of K⁺ ions into the voids enclosed by the NiN₆ and CrC₆ octahedra, which was used to understand the appearance of photoenhanced ferromagnetism in the K–Ni–Cr network. A weak moment developed in the core below 10 K, corresponding to separate ordering of the Co and Fe ions in the Rb–Co–Fe network. Photoinduced ferromagnetism of the Co and Fe ions in the Rb–Co–Fe was also detected.

1. INTRODUCTION

Prussian blue analogues (PBAs) demonstrate many fascinating magnetic behaviors. In this study, we examine PBAs, with the general chemical formula of AₓM[M’(CN)₆₋ₓ]ₓ₋ₙH₂O (A–M–M’), where M and M’ indicate divalent and trivalent transition-metal ions, respectively, and A indicates monovalent alkali ions that are accommodated in the voids enclosed by the MN₆ and M’C₆ octahedra. Their magnetic characteristics are dependent on the intrinsic nature of the complexes but can also be greatly altered by extrinsic stimulation, such as the application of pressure or light irradiation.1–12 In particular, one very promising characteristic is the photoinduced magnetism found in A–Co–Fe (with A = K, Na, Rb, and Cs), which has been demonstrated to be sensitive to the type and the amount of A⁺ ions that have been incorporated into the compound.1,2,6 This behavior is believed to originate from the electron transfer that occurs between the MN₆ and M’C₆ octahedra, known as the charge-transfer-induced spin transition (CTIST).13–15 It has been shown that a significant reduction in magnetization occurs as a consequence of light irradiation in layered Rb–Ni–Cr/Rb–Co–Fe/Rb–Ni–Cr heterostructures composed of a photosensitive Rb–Co–Fe film sandwiched between two pressure-sensitive Rb–Ni–Cr films.16,17 This reduction is believed to be a direct result of the weakening of the atomic connections between the CoN₆ and FeC₆ octahedra, caused by the lattice expansion of the Rb–Co–Fe layer driven by the strain that builds up at the interfaces as a consequence of light irradiation. In addition, the magnetic response of nanosized core/shell heterostructures has recently been found to be sensitive to the shell thickness.18–22 No photoinduced magnetism has been identified in isolated K–Ni–Cr, but light irradiation leads to a noticeable reduction (~8%) of the magnetization when this material is coated on a Rb–Co–Fe nanocube.18 This reduction is understood to be linked to the structural distortion that occurs in the K–Ni–Cr, triggered by the stress that develops in the photoactive Rb–Co–Fe. Clearly, the photomagnetic sensitivity of PBA can be tuned by adjusting the chemical composition and stress of these complexes. In this study, we aim to develop K–Ni–Cr PBAs, where light irradiation will enhance, rather than reduce, the magnetic strength of the compound. We demonstrate that K–Ni–Cr can become photoactive in high-K⁺-containing compounds. We detected significant increases of the Ni and Cr magnetic moments upon UV-light irradiation in a 55 nm thick high-K⁺-containing K–Ni–Cr shell coated on a 240 nm Rb–Co–Fe cube (hereafter Rb–Co–Fe@K–Ni–Cr). Surprisingly, the photoenhancement of the magnetic moments for the K₀.₉₈–Ni–Cr₀.₇₀ phase was as large as that for the Rb₀.₇₆–Co–Fe₀.₇₄ phase. The better photomagnetic sensitivity in the present K–Ni–Cr PBA network was obtained by the incorporation of a large amount of K⁺ ions into the compound, leading to a greater electron distribution near the bridging C–N ions, which strengthened the electronic connections in the Ni–N–C–Cr–C–N–Ni chains.

Received: May 7, 2017
Accepted: July 21, 2017
Published: August 4, 2017

DOI: 10.1021/acsomega.7b00565
ACS Omega 2017, 2, 4227–4236
2. MATERIALS AND METHODS

2.1. Sample Fabrication. The core@shell PBA heterostructures, with the Rb–Co–Fe phase at the core and the K–Ni–Cr phase on the shell, were synthesized by the coprecipitation method. The core particles Rb–Co–Fe were prepared by adding 330 mL of an aqueous solution containing particles were subsequently washed and redispersed in 100 mL of pure water. This process followed by the addition of 200 mL of pure water, and stirred for 18 h. The microcrystalline powder was isolated from the solution by centrifugation and then rinsed three times with pure water. For the synthesis of Rb–Co–Fe@K–Ni–Cr particles, previously prepared core particles were dispersed in 200 mL of pure water, followed by the addition of 150 mL of aqueous solution containing 1.1 mmol K3Fe(CN)6. The mixture was then slowly stirred for 18 h. The microcrystalline powder was isolated from the solution by centrifugation and then rinsed three times with pure water. The synthesis of Rb–Co–Fe@K–Ni–Cr particles was accomplished in three cycles. We note that the M ions in PBA crystals with a general chemical formula of A\textsubscript{M}M′(CN)\textsubscript{y}·nH\textsubscript{2}O will form a face-centered cubic sublattice allowing the accommodation of either M′(CN)\textsubscript{y} or (H\textsubscript{2}O)\textsubscript{z} between the two M ions along the three crystallographic axis directions, giving rise to a stoichiometric composition of M′(CN)\textsubscript{y}+(H\textsubscript{2}O)\textsubscript{z}. In addition, the voids enclosed by the MN\textsubscript{x} and M\textsubscript{C}o octahedra can accommodate either alkali A ions or H\textsubscript{2}O molecules or be left empty, giving rise to a stoichiometric composition of A\textsubscript{M}(H\textsubscript{2}O)\textsubscript{x}. For the Rb–Co–Fe@K–Ni–Cr particles, a constrained stoichiometric composition of A\textsubscript{M}(H\textsubscript{2}O)\textsubscript{x} with x + z ≤ 1, for each of the PBA phases was used for pattern refinement. Crystalline analysis was then carried out for the determination of the stoichiometric compositions (x, y, z) for each phase and the atomic positions of C, N, and the two separate O ions (one in the 8c sites and the other bound to the M ions) in the unit cell.

2.2. Instrumentation. X-ray diffraction (XRD) measurements were performed on a Bruker D8 ADVANCE diffractometer, employing the standard setup for reflection geometry. Neutron diffraction measurements were conducted at the Bragg Institute, Australian Nuclear Science and Technology Organisation (ANSTO), Australia, using the high-intensity powder diffractometer Wombat, employing a highly collimated beam. For these measurements, 1 g of the sample was loosely loaded into a cylindrical aluminum holder (9 mm in diameter and 30 mm in length) with a shiny inner surface. The device was equipped with a quartz tube (5 mm in diameter) located along the central axis of the holder to facilitate light irradiation. The PBA powder was loosely packed (2 mm thick) in the quartz tube, allowing 35% light transmission, which, combined with the shiny inner face of the Al holder that acted as a light reflector, allowed the light to bounce back and forth inside the holder for uniform illumination of the PBA sample. The sample temperature was controlled using a He gas refrigerator system. The magnetization and alternating current (ac) magnetic susceptibility measurements were performed on a physical property measurement system (PPMS), manufactured by Quantum Design, Inc., employing the standard setups. For these measurements, ~80 mg of the sample was loosely packed into a thin nonmagnetic cylindrical holder that produced a smooth temperature curve with a background signal that was ~2% of the strength of the signal from the sample. The powdered sample was shaken at 50 Hz for 5 min using a Vortex-Genie mixer to avoid aggregation among the nanoparticles. The mass density was 1.6% of the bulk density, which corresponds to an average interparticle separation from edge to edge of 2.6 times the particle diameter so that the interparticle interaction would be insignificant.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition. The crystalline structure and stoichiometric parameters were determined by combining and cross-checking of profile refinements of the X-ray and neutron diffraction patterns. XRD measurements were first used to construct the backbone of the crystalline structure. Neutron diffraction was then used to identify the atomic positions and the stoichiometric amounts of the transition-metal ions and H\textsubscript{2}O molecules within the compound. It is known that the M ions in PBA crystals with a general chemical formula of A\textsubscript{M}M′(CN)\textsubscript{y}·nH\textsubscript{2}O will form a face-centered cubic sublattice allowing the accommodation of either M′(CN)\textsubscript{y} or (H\textsubscript{2}O)\textsubscript{z} between the two M ions along the three crystallographic axis directions, giving rise to a stoichiometric composition of M′(CN)\textsubscript{y}+(H\textsubscript{2}O)\textsubscript{z}. In addition, the voids enclosed by the MN\textsubscript{x} and M\textsubscript{C}o octahedra can accommodate either alkali A ions or H\textsubscript{2}O molecules or be left empty, giving rise to a stoichiometric composition of A\textsubscript{M}(H\textsubscript{2}O)\textsubscript{x}. For the Rb–Co–Fe@K–Ni–Cr particles, a constrained stoichiometric composition of A\textsubscript{M}(H\textsubscript{2}O)\textsubscript{x} with x + z ≤ 1, for each of the PBA phases was used for pattern refinement. Crystalline analysis was then carried out for the determination of the stoichiometric compositions (x, y, z) for each phase and the atomic positions of C, N, and the two separate O ions (one in the 8c sites and the other bound to the M ions) in the unit cell. Our structural analysis began with profile refinement of the XRD pattern, with a focus on obtaining the stoichiometric composition x, with the occupancies of C and N being constrained as the same as the associated Fe or Ni, but ignoring the existence of H. The fit can be greatly improved by refining the neutron diffraction patterns, beginning with the structural parameters obtained from the X-ray results, but focusing on refining y, z, and the positions of H. The structural parameters thus obtained were once again fed back into the X-ray patterns for further refinement of x and again to the neutron patterns for further refinement of the y, z, and H\textsubscript{2}O parameters. The structural parameters were then converged after three cycles of refinement analysis, combining the X-ray and neutron results.

The diffraction patterns were analyzed using the Rietveld method, employing the general structure analysis system (GSAS) program. Two separate structural phases with the same cubic Fm\textsubscript{3}m symmetry can be identified in each diffraction pattern, one belonging to the Rb–Co–Fe phase and the other to the K–Ni–Cr phase. The observed and calculated X-ray and neutron diffraction patterns at 80 K are shown in Figure 1a,b, respectively. The chemical compositions obtained for the two phases after final refinement were Rb\textsubscript{0.76}Co\textsubscript{0.24}Fe\textsubscript{0.74}(H\textsubscript{2}O)\textsubscript{0.26}·0.56H\textsubscript{2}O with a cubic lattice constant of a = 9.943(2) Å and K\textsubscript{0.98}Ni\textsubscript{0.02}(Cr\textsubscript{0.70}(H\textsubscript{2}O)\textsubscript{0.30}·0.11H\textsubscript{2}O with a = 10.337(4) Å at 80 K. The mass ratio of the Rb–Co–Fe to K–Ni–Cr phases obtained from the fit was 57:43. The refined structural parameters of the two phases at 300, 80, and 3 K are summarized in Tables 1, 2, and 3, respectively. We note that refinement imposes constraints on the charge balance, thus imposing ionic states of A\textsuperscript{+}, M\textsuperscript{+}, and M\textsuperscript{2+}, and results in unacceptable negative occupancies for the A sites in both phases or almost fully occupied M\textsuperscript{+} sites for both phases but with a very poor fit (χ\textsuperscript{2} = 2.85, R\textsubscript{wp} = 2.38%, and R\textsubscript{wp} = 3.49% constraints; χ\textsuperscript{2} = 1.26, R\textsubscript{wp} = 1.79%, and R\textsubscript{wp} = 2.32% without constraints). Rb\textsubscript{0.76}Co\textsubscript{0.24}Fe\textsubscript{0.74}(H\textsubscript{2}O)\textsubscript{0.26}·0.56H\textsubscript{2}O and K\textsubscript{0.98}Ni\textsubscript{0.02}(Cr\textsubscript{0.70}(H\textsubscript{2}O)\textsubscript{0.30}·0.11H\textsubscript{2}O obtained for the present compound indicate that portions of the Co and Ni ions are in the M\textsuperscript{2+} ionic state at 80 K. The bond valence calculations give bond valence sums of 2.93 and 2.97 for the Co and Ni ions, respectively, at 80 K. In addition, the X-ray photoelectron spectrum (XPS) reveals a binding energy of 578.5 eV for the Cr 2p\textsubscript{3/2} line (Figure 2), which differs from the 576.5 eV for the Fe 2p\textsubscript{3/2} line in the starting...
material K₃Cr(CN)₆ and the 576.7 eV for the Cr₃⁺ 2p½½ line in Mn₃₇₄₋₄(Cr(CN))₆·₃H₂O vs Ni₃₇₄₋₄(Cr(CN))₆·₃H₂O PBA, but is close to the 578.1 eV of the Cr⁺² 2p½½ line in CrF₂. Apparently, a reduction of the Cr valence from the Cr³⁺ in K₃Cr(CN)₆ does occur during fabrication process. On the other hand, the binding energy of the Fe 2p½ line is not clearly revealed in the XPS results, reflecting the attenuation of the XPS signal from the Rb–Co–Fe phase in the core.

The crystalline structure of the PBA can be viewed as being composed of MN₆ and M′C₆ octahedra that are alternately linked to form M–N–C–M′–C–N–M chains along all three crystallographic axis directions. This structure opens up channels among the chains, with A⁺ ions or H₂O accommodated in the voids, as shown in Figure 3. A relatively large amount of K (~50%) occupies the voids in the K–Ni–Cr phase on the shell, but less amount of Rb (~38%) for the Rb–Co–Fe phase in the core. There were no identifiable traces of impurity phases in the neutron or XRD patterns. No structural symmetry change was detected between 450 and 3 K, as the same cubic Fm3m crystalline symmetry was maintained in both the Rb–Co–Fe and K–Ni–Cr phases in this temperature range.

3.2. Structural Conformation. Transmission electron microscopy (TEM) images (insets to Figure 4a) revealed the presence of core@shell nanocubes, rather than spherical nanoparticles, in the compound. The size distribution, calculated from the TEM images, reveals the nanocubes to have a mean diameter of d = 350 nm (Figure 4a), with 90% of the cubes in the assembly having an edge length in the range of 350 ± 50 nm. Composition scans, employing a beam spot 22 nm in size, of the nanocubes revealed no Co but Ni at the edges, which penetrated 44 nm into the nanocubes (Figure 4b). In other words, there is a 44 nm wide region, where the Ni composition decreases and the Co composition increases toward the interior of the nanocubes. It is important to note that this does not indicate the appearance of an interfacial layer where the two phases mix together, but a direct result of scanning the beam spot through the interface. The thickness of the shell is calculated to be 44 ± (22/2) = 55 nm. The compositions of both Ni and Co stabilize about 66 nm deep into the nanocubes. It is clear that the core@shell nanocubes are composed of Rb–Co–Fe cubic cores with a mean edge length of 240 nm covered by K–Ni–Cr shells with a mean thickness of 55 nm. This result agrees reasonably well with the mass ratio of 55% for the Rb–Co–Fe phase and 45% for the K–Ni–Cr phase obtained from the neutron diffraction measurements.

3.3. Negative Thermal Expansion (NTE). A dramatic change to significantly smaller unit cells of the Rb–Co–Fe phases appeared upon cooling to 280 K (Figure 5a). This large shrinkage of the Rb–Co–Fe unit cells upon cooling goes beyond what can be accounted for by strengthening of the lattice anharmonicity. Rather it has been suggested that it is associated with the occurrence of CTIST. No such CTIST-

| Table 1. List of the Refined Structural Parameters of the Core@Shell PBA at 300 K, Where Biso Represents the Isotropic Temperature Parameter |
|-----------------|-------|-------|-------|-----------------|
| atom            | x     | y     | z     | Biso (Å²)       | occupancy |
| Rb              | 0.25  | 0.25  | 0.25  | 8c              | 6.3(9)    | 0.38(1) |
| Co              | 0.5   | 0.5   | 0.5   | 4b              | 2.1(7)   | 1       |
| Fe              | 0     | 0     | 0     | 4a              | 5.8(9)   | 0.74(2) |
| C               | 0.214(2) | 0   | 0     | 24e             | 1.7(7)   | 0.74(2) |
| N               | 0.322(3) | 0   | 0     | 24e             | 2.5(6)   | 0.74(2) |
| O(1)            | 0.232(9) | 0  | 0     | 24e             | 3.6(9)   | 0.26(2) |
| H(1)            | 0.288(8) | 0.055 | 0.055 | 96k             | 2.8(8)   | 0.13(3) |
| O(2)            | 0.25  | 0.25  | 0.25  | 8c              | 3.3(9)   | 0.28(3) |
| H(2)            | 0.194 | 0.194 | 0.194 | 32f             | 43.5(5)  | 0.14(5) |

*Occupancies of C and N are constrained to be the same as the associated Fe or Ni. Specific occupancy of H is constrained to be half that of the associated O.
related unit-cell shrinking was detected for the K–Ni–Cr phase upon cooling to 3 K, but revealing noticeable increases in the widths of the diffraction peaks along with the thermal shifts of the peak positions upon warming to above 150 K for the Ni–Ni–Cr phase (Figure 5a). Interestingly, the increase in the {400} intensity of the Rb–Co–Fe phase upon cooling through the transition was accompanied by a decrease in the {400} intensity of the K–Ni–Co phase (Figure 5a). Similar changes of the diffraction intensities were also observable28 by XRD. There were no obvious anomalies found in the thermal variations of the magnetization or magnetic susceptibility through the transition, measured employing the PPMS magnetometer. The thermally induced changes in the diffraction intensities through the transition were mainly structural, rather than magnetic, in origin. In addition, NTE, where lattice shrinks upon warming, of the K–Ni–Cr phase appears above 30 K (Figure 5b). No NTE was found for the Rb–Co–Fe phase. These XRD patterns were taken from 300 K, employing a low warming rate (∼1 K/min) when temperature changes were initiated. The NTE observed for the K–Ni–Cr phase is intrinsic because it begins to appear at a relatively low temperature of 320 K, where loss of H2O from the compound is unlikely to occur.

3.4. Magnetic Transitions. Two magnetic transitions, labeled $T_{\text{m1}}$ and $T_{\text{m2}}$, are clearly revealed in the isofield direct current magnetization $M(T)$ and ac magnetic susceptibility $\chi'(T)$ curves (Figure 6a). There is a large increase in the magnetization upon cooling to below $T_{\text{m1}} = 72$ K, which is linked to the magnetic ordering of the Ni and Cr ions in the K–Ni–Cr phase on the shell. At 30 K, the Ni spins together with the Cr spins developed a ferromagnetic arrangement with magnetic moments of $\langle \mu_2 \rangle_{\text{Ni}} = 0.93(9)\mu_B$ and $\langle \mu_2 \rangle_{\text{Cr}} = 1.50(9)\mu_B$ pointing along the [111] crystallographic direction at 30 K (Figure 6b). This magnetic diffraction pattern is indicative of the additional intensity that developed upon cooling from 80 to 30 K. It is analyzed employing the GSAS

![Figure 2. XPS in the range of the Cr 2p state, revealing a binding energy of 578.5 eV for the Cr 2p2/3 line and a satellite at 588 eV. The arrows indicate the expected binding energy of the Cr 2p2/3 line in the K$_6$Cr(CN)$_6$·nH$_2$O starting material and in Mn$_{1.5}$[Cr(CN)$_6$]$_{n}$H$_2$O@Ni$_{1.5}$[Cr(CN)$_6$]$_{n}$H$_2$O.

DOI: 10.1021/acsomega.7b00565

ACS Omega 2017, 2, 4227–4236
program, assuming the same spatial symmetry of the crystalline structure for the magnetic structure. It is interesting to note that the magnetic response (\(\chi^\prime\)) associated with the transition at \(T_{m1}\) was largely suppressed by the applied magnetic field. An \(H_a\) as weak as 200 Oe leads to a decrease in \(\chi^\prime\) response by as much as 1 order of magnitude. This reflects the known glassy nature of the nonstoichiometric PBAs, rather than the antiferromagnetic character of the transition at \(T_{m1}\). The \(M(\theta)\) and \(\chi^\prime(\theta)\) curves reveal slightly but noticeably larger values of \(M\) and \(\chi^\prime\) below \(T_{m2} = 10\) K (Figure 6a), which are linked to the magnetic ordering of the Co and Fe ions in the Rb–Co–Fe phase in the core. Interestingly, \(M\) and \(\chi^\prime\) decreased with decreasing temperature below 7 K. These measurements were performed in warming processes, after zero-field cooling from 300 to 1.8 K and a wait time of 30 min. It revealed the thermal agitation of the magnetic-order parameter. The thermal behavior of \(M\) below 10 K is currently not completely understood. It is known that increases of \(M\) and \(\chi^\prime\) can occur upon warming from a low temperature in situations where a residual field appears in the zero-field process, if the residual field is sufficient to cause alignment of the Ni–Cr domains but not small to align all of the Co–Fe domains. However, a residual field of 15 Oe, judging from the \(M(H_a)\) curve taken at 2 K, would be required to account for the 0.7 emu upturn revealed in the \(M(\theta)\) curve at temperatures below 7 K. It is unlikely that such a high

Figure 3. Schematic drawing of the proposed crystalline structure of the Rb–Co–Fe in the core and the K–Ni–Cr shell. This structure can be viewed as consisting of Co–N–C–Fe–C–N–Co chains in the core and Ni–N–C–Cr–C–N–Ni chains in the shell along the three crystallographic axis directions. The atomic deficiencies revealed in the plot are for the K0.98Ni0.02 phase.

Figure 4. (a) Size distribution of the nanocube assembly obtained from the TEM images, revealing a mean edge length of 350 nm for the assembly. The insets show representative TEM images of the PBA heterostructure, revealing the core@shell structure of the nanocubes. The horizontal bar indicates 100 nm. (b) Mean Co and Ni compositions of the Rb–Co–Fe@K–Ni–Cr PBA nanocubes at positions across the nanocubes from the edge.

Figure 5. Stack plots of the \{400\} diffraction peaks obtained by (a) neutron diffraction from 10 to 300 K and (b) XRD from 300 to 450 K. Dramatic changes of the Rb–Co–Fe unit cell appear around 280 K, and NTEs of the K–Ni–Cr unit cell appear above 280 K.
residual field did appear. One possible source would be that the magnetic moments in the Rb–Co–Fe core and on the K–Ni–Cr shell point in opposite directions, causing the appearance of a spiral moment arrangement in the interfacial layer. The increase in $M$ on warming from a low temperature is a result of the weakening of the moments in the Rb–Co–Fe core, whereas the decrease in $M$ above 7 K reflects the weakening of the moments in the interfacial layer. These small changes in $M$ are beyond the current capability of the neutron diffraction to monitor.

3.5. Photomagnetic Sensitivity. It is remarkable to see that the magnetic moments of both the K–Ni–Cr and Rb–Co–Fe phases increase significantly upon continuous irradiation with 365 nm UV light at 2.5 mW during the measurement, as revealed by the large increases of the neutron magnetic intensities associated with both phases (Figure 7). Photoinduced magnetism has been observed in Rb–Co–Fe\textsuperscript{16} but has not yet been detected in K–Ni–Cr complexes. Surprisingly, the magnetic phase of K–Ni–Cr is more sensitive to light irradiation than that of Rb–Co–Fe, as reflected by the increase in the representative (200) magnetic intensity of the

![Figure 6](https://example.com/figure6.png)  
**Figure 6.** (a) Temperature dependence of the magnetization $M$ of the PBA assembly, measured employing an applied magnetic field of $H_0 = 300$ Oe. Temperature dependence of the in-phase component $\chi'$ of the ac magnetic susceptibility, measured employing a driving ac magnetic field with a root-mean-square strength of 10 Oe and a frequency of 37 Hz. Two anomalies at $T_{m1} = 72$ K and $T_{m2} = 10$ K are revealed. (b) Magnetic intensities observed at 30 K, where the neutron diffraction intensities observed at 80 K, which serve as the nonmagnetic background, have been subtracted. The solid curves indicate the calculated magnetic intensities based on the proposed spin arrangement. The solid vertical lines mark the calculated positions of the magnetic Bragg reflections of the proposed spin arrangements for the K–Ni–Cr (top series) and Rb–Co–Fe (bottom series).

![Figure 7](https://example.com/figure7.png)  
**Figure 7.** Difference in intensities between the neutron diffraction patterns taken with and without light irradiation at 3 K. The magnetic intensities associated with the K–Ni–Cr and Rb–Co–Fe phases are revealed. The solid curves indicate the calculated magnetic intensities based on the proposed spin arrangement. The solid vertical lines mark the calculated positions of the magnetic Bragg reflections of the proposed spin arrangements for the K–Ni–Cr (top series) and Rb–Co–Fe (bottom series).

K–Ni–Cr phase, which is 1.7 times larger than that of the Rb–Co–Fe phase. We note that the mass of the K–Ni–Cr phase in the compound is only 80% that of the Rb–Co–Fe phase. It is known that the magnetic intensity is primarily linked to the magnetic form factor and magnetic moment.\textsuperscript{29} The magnetic form factors of the Ni\textsuperscript{2+}, Cr\textsuperscript{3+}, Co\textsuperscript{2+}, and Fe\textsuperscript{3+} spins in the (200) scattering regime are comparable (0.90–0.92),\textsuperscript{30} and the moment direction does not greatly affect the magnetic intensity in high-symmetry cubic crystals. It is the magnitude of the magnetic moment that develops upon light irradiation, which gives rise to the increase in the magnetic intensities. It appears that the magnetic diffraction pattern enhanced by the UV-light irradiation (Figure 7) is different from that obtained by cooling (Figure 6b). In particular, the UV-light irradiation produces a much more intense (111) magnetic reflection, showing that the irradiation generates different amounts of magnetic moments for the Ni and Cr ions. This is understandable because the Ni and Cr ions are in different magnetic states. There is no structural symmetry change or lattice distortion induced by the UV-light irradiation that may be identified from the neutron diffraction patterns. However, neutron diffraction patterns do reveal noticeable changes in the atomic positions, especially for C and N, after irradiation (Tables 3 and 4). The Cr–C and Fe–C separations reduce by ~2.8 and ~2.2%, respectively, whereas the Ni–N and Co–N separations increase by ~2.5 and ~1.9%, respectively, after UV-light irradiation. In addition, expected\textsuperscript{20} changes in the lattice constants upon light irradiation will not be revealed in the present neutron diffraction patterns, which are focused on intensity but relaxed in resolution. The magnetic moments of the Ni and Cr ions increase by 0.23 and 0.32$\mu_B$, respectively, upon irradiation with 365 nm UV light at 2.5 mW, assuming that the moment directions and crystalline structure remain unaltered. Correspondingly, magnetic moments of 0.26(1)$\mu_B$ for the Co ions and 0.19(2)$\mu_B$ for the Fe ions are found to develop. Photoirradiation drives the Cr ions from in the S = 1 to 3/2 magnetic state and the Ni ions from in the $S = 1/2$ to 1 magnetic state. The increases in the magnetic moments of 0.32 and 0.23$\mu_B$ for Cr and Ni ions, respectively, correspond to 32%
of the Cr ions being photoactive, with only 0.23/0.32 = 72% of the electron transfer reaching the Ni ions. On the other hand, photoradiation drives the nonmagnetic Fe and Co ions into the $S = 1/2$ and $3/2$ magnetic states, respectively. The increases in the magnetic moments of 0.19 and 0.26 compared to the compound discussed in the present study is quite different from that of the K0.36–Ni–Cr0.74 reported in ref 31. The distribution of the electronic charge appeared between the two Cr–Cr nearest neighbors along the [110] crystallographic direction (Figure 8). We note that a higher-K$^+$-containing compound will generate less intense (200) X-ray reflections together with more intense (220) X-ray reflections. The intensity ratios between the (200) and (220) X-ray reflections observed in the present compound and in the one reported in ref 31 are 1.53 and 1.71, respectively (Figure 8). The chemical composition of the compound discussed in the present work is Rb$_{0.76}$Co–Fe$_{0.74}$@K$_{0.98}$Ni–Cr$_{0.74}$ whereas the one reported in ref 31 has a chemical composition of Rb$_{0.48}$Co–Fe$_{0.74}$@K$_{0.36}$Ni–Cr$_{0.74}$. The appearance of more K$^+$ ions in the voids enclosed by the NiN$_6$ and CrC$_6$ octahedra will supply more electronic charges to their neighboring atoms so that a higher electronic charge distribution around the Ni–N–C–Cr–C–N–Ni chains can be anticipated. In one study, a 0.5% increase in the magnetization contributed from the shell after light irradiation in Rb$_{0.5}$–Co–Fe$_{0.5}$@Rb$_{0.5}$–Ni–Cr$_{0.74}$ PBA was reported. However, the A sites are much less occupied and the thickness of the shell was much less for the compound reported in ref 20 compared to the compound discussed in the present study. Photomagnetic activity can be sensitive to the size of the compound. Apparently, the relatively high photomagnetic sensitivity for the K–Ni–Cr phase in the present compound not only links to the high K composition but size may also play a crucial role. In addition, large increases in the magnetization and coercive field, as a consequence of light irradiation, have also been reported in Cs$_{0.5}$–Ni–Fe$_{0.5}$@Cs$_{0.5}$–Co–Fe$_{0.5}$, where the insertion of Cs$^+$ ions has been demonstrated to be essential for efficient photomagnetic activity.

### 3.6. Electronic Charge Distribution

Remarkably, the electronic charge distribution of the K$_{0.98}$–Ni–Cr$_{0.74}$ discussed in the present work is quite different from that of the K$_{0.36}$–Ni–Cr$_{0.74}$ reported in ref 31. The distribution of the electronic charge density in the Ni–N–C–Cr chains in the present K$_{0.98}$–Ni–Cr$_{0.74}$ is noticeably widely extended, and a greater electronic charge appeared between the two Cr–Cr nearest neighbors along the [110] crystallographic direction (Figure 9a,b). These electron-density maps were obtained by employing...
ing the GSAS program, starting with profile refinement of the XRD patterns, followed by calculation of the inverse Fourier transforms of the structure factors to extract the electron-density distribution. The electron-density contour map of a specific plane was then obtained by slicing the electron density in the vicinity of the specific plane, including 0.025 Å below and above it.

It is clear that the amount of K+ ions incorporated into the compound can significantly alter the electronic charge distribution. These changes are better revealed in the difference density plots, where the electron density of the K_{0.98}−Ni−Cr_{0.70} reported in ref 31 is subtracted from that of the present compound, including 0.025 Å below and above it.

Figure 9. Electronic charge densities in the (0 0 0.05) crystallographic plane of (a) the present Rb_{0.76}−Co−Fe_{0.74}@K_{0.98}−Ni−Cr_{0.70} and (b) the Rb_{0.48}−Co−Fe_{0.74}@K_{0.36}−Ni−Cr_{0.74} reported in ref 31, as inferred from the XRD data. The color bars are in units of e/Å$^3$.

Figure 10. Differences in the electronic charge density between the present Rb_{0.76}−Co−Fe_{0.74}@K_{0.98}−Ni−Cr_{0.70} and the Rb_{0.48}−Co−Fe_{0.74}@K_{0.36}−Ni−Cr_{0.74} reported in ref 31 in the (a) (0 0 0), (b) (0 0 0.05), and (c) (0 0 0.08) crystallographic planes. The atomic positions with negative difference density values represent the locations where electronic charges are less in the present compound but redistributed to the positions with positive values. The color bars are in units of e/Å$^3$.

Cr ions can then be anticipated. An increase of the electronic charge density between the two nearest Ni−Ni ions along the [110] crystallographic direction is also evident. Interestingly, the outer electronic charges of the C ions at (0.199 0 0) increase largely but distributed toward the N ions at (0.323 0 0) (Figure 10a,b). In addition, the outer electronic charges of the Cr ions (Figure 10b,c), Ni ions (Figure 10a,c), and N ions (Figure 10b,c) are more extended/distributed. A better electronic connection along the Ni−N−C−Cr−C−N−Ni chains can thus be anticipated in the high-K+−containing compounds (Figure 10c).
3.7. Possible Mechanisms. The photoinduced magnetism observed in the A−Co−Fe PBAs is understood to originate from the charge transfer occurring between the Fe and Co ions, triggered by light irradiation, transferring the nonmagnetic Co$^{3+}−$N−C−Fe$^{2+}$ configuration into the magnetic Co$^{2+}−$N−C−Fe$^{3+}$ one. The main mechanism behind the photoenhanced ferromagnetism in the K−Ni−Cr network is not completely understood at this time. The weakening of the magnetic coupling induced by the stress that builds up at the interface in the Rb−Co−Fe@K−Ni−Cr compound, which has been reported in ref 17, does not appear in the present study. There was no significant change in the lattice constant following UV-light irradiation found in either the Rb−Co−Fe or K−Ni−Cr phase, where the lattice constant of Rb−Co−Fe changed from 9.942(2) to 9.939(2) Å and that of K−Ni−Cr changed from 10.332(4) to 10.334(4) Å. Light irradiation does result in significant shrinkages of the C−Cr and C−Fe separations together with large enlargements of the Ni−N and Co−N separations. It appears that the N−C blocks shift toward Cr or Fe ion. The origin for the absence of a change in lattice constant upon light irradiation can be linked to that the wavelength of the light is not appropriate and/or that only there are small amounts of Co and Fe ions that are photoactive (32% for Co and 19% for Fe). Structural analysis assuming Fe−C−N−Co chains in the Rb−Fe−Co phase and Ni−C−N−Cr chains in the K−Ni−Cr phase results in a very poor fit ($χ^2$ = 7.233, $R_p$ = 2.15%, and $R_wp$ = 2.82%) with unacceptable negative occupancies for the A sites in both phases. In particular, it generates an intensity for the (111) reflection that is 230% of the observed one. Refinements allowing both coordination isomers to appear in both phases give small fractions for the Fe−C−N−Co (4.5%) and Ni−C−N−Cr (5.3%) chains. Cyanide coordination isomerism is unlikely the dominant factor for the observed photoenhanced ferromagnetism in the K−Ni−Cr network. One possible source for the photoenhanced ferromagnetism in the K−Ni−Cr is the direct excitation from the $t_{2g}$ to $e_g$ orbitals of the Cr ions in the CrO$_6$ octahedra and the Ni ions in the NiN$_6$ octahedra by the UV-light irradiation. This, however, would lead to the transfer of Cr ions from the $S$ = 1 to 2 magnetic state and the Ni ions from the $S$ = 1/2 to 3/2 magnetic state, which would give rise to much larger increases in the Cr and Ni magnetic moments than the 34 and 15% increases, respectively, observed in the present study, if all of the Ni and Cr ions are excited. In addition, bond valence calculations, based on the structural parameters obtained from the neutron diffraction patterns, show that the bond valence of the Ni ions in K$_{0.98}$−Ni−Cr$_{0.70}$ changes from +2.79 to +2.23 upon irradiation by UV light, whereas that of the Co ions in Rb$_{0.70}$−Co−Fe$_{0.27}$ changes from +2.73 to +2.33. It has been pointed out that the insertion of low alkali cations around the M ions so that more M ions will undergo a change in spin accompanied by electron transfer to $[\text{M}^2(\text{CN})_6]^{3-}$ upon cooling or photoirradiation. The relatively high K composition in the present K$_{0.98}$−Ni−Cr$_{0.70}$ provides more electronic connections along the Ni−N−C−Cr chains, leading to greater photoinduced charge transfer along the chains upon cooling or photoirradiation. Relatively small magnetic moments were developed for the Ni (0.93$\mu_B$) and Cr (1.50$\mu_B$) ions upon cooling, reflecting a relatively weak superexchange coupling between the Ni and Cr ions. The enhanced ferromagnetism for the K−Ni−Cr network by UV-light irradiation can be a result of enhanced superexchange coupling between the Ni and Cr ions mediated through the bridging N−C ions.

4. CONCLUSIONS

A nanosized Prussian blue core@shell heterostructure with a 240 nm Rb$_{0.70}$Co[$\text{Fe(CN)}_6]$$_{0.74}$($\text{H}_2\text{O}$)$_{1.26}$0.56H$_2$O core covered by a 55 nm K$_{0.98}$Ni[Cr(CN)$_6$]$_{0.70}$($\text{H}_2\text{O}$)$_{6.30}$0.11H$_2$O shell was synthesized by the coprecipitation method. A relatively high K composition was incorporated into the compound by employing a denser K$_2$[Cr(CN)$_6$] aqueous solution during the preparation process. Two magnetic transitions at 10 and 72 K were identified. The transition at 10 K is linked to the ferromagnetic ordering of the Co and Fe ions in the Rb−Co−Fe phase. The magnetic moments of Co and Fe were greatly enhanced by UV-light irradiation as detected through neutron diffraction. The thermal CTIST could barely be seen in the Rb−Co−Fe phase, but charge transfer could be triggered by optical excitation to reveal the magnetic state. The transition at 72 K is linked to the ferromagnetic ordering of the Ni and Cr spins in the K−Ni−Cr phase. Significant increases of the Ni and Cr magnetic moments (34 and 15%, respectively) were found after photoirradiation by 365 nm UV light at 2.5 mW. The photoenhanced ferromagnetic strength is understood to be linked to the direct excitation from the $t_{2g}$ to $e_g$ orbitals of the Cr and Ni ions and/or the enhanced superexchange coupling between the Ni and Cr ions, made possible by the incorporation of more K$^+$ ions into the compound, allowing for a higher degree of electronic connectivity along the Ni−N−C−Cr−N−Ni chains. It is the high K$^+$ in the compound together with UV radiation excitation that triggers the enhanced ferromagnetism in K$_{0.98}$−Ni−Fe$_{0.27}$ PBAs.

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ACKNOWLEDGMENTS

The authors thank ANSTO for providing the neutron beam time and the light illumination device that made the neutron diffraction measurements possible. This work was supported by the Ministry of Science and Technology of Taiwan under Grant No. MOST 104-2112-M-008-007-MY3.

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