

Article

Positive and Negative Exchange Bias in *N*-, *P*- and *Q*-Type Ferri-Magnets of Niccolite Metal Formates $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{1-x}\text{Fe}^{\text{III}}_x\text{Fe}^{\text{II}}(\text{HCO}_2)_6]_n$

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Abstract: Exchange bias (EB) materials, whose magnetization curve can shift along the field axis after field cooling, have attracted tremendous attention and play a crucial role in the development of fundamental physics as well as practical applications of magnetization storage. In this work, the *N*-, *P*-, and *Q*-type ferrimagnets of Néel's notation were realized in mixed valence metal formates $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{1-x}\text{Fe}^{\text{III}}_x\text{Fe}^{\text{II}}(\text{HCO}_2)_6]_n$ by altering *x*, respectively. The positive and negative EB was found in *N*- and *P*-type ferrimagnets. The exchange anisotropy originates from the antiferromagnetic exchange interaction between the uncompensated spin of the host ferrimagnetic lattice and the pinned compensated spin of the antiferromagnetic clusters as a guest, which is rooted in the valence disorder of the iron ions.



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1. Introduction

The exchange bias (EB) effect, namely a shift of the magnetization curve along the field axis after field cooling, plays a crucial role in the development of fundamental physics as well as practical applications of magnetization storage [1–3]. It is generally believed that the phenomenon of EB originates from the exchange coupling between ferromagnetic (FM) and anti-ferromagnetic (AFM) interfaces, which leads to another magnetic field (H_i) distinct from the applied field (H_a) [4]. Therefore, the attention of the relative researchers has mainly been focused on the construction of the FM/AFM bilayer systems [5]. As a result, in a negative EB field, the magnetization curve shifting in the direction against that of the cooling field is a usual experimental observation despite the nature of the FM–AFM interaction [6].

However, a positive EB phenomenon has been found in some systems, i.e., TM/TMF₂ (TM = transition metal) layers [7], which surpasses the simple picture of mechanisms presented by FM/AFM bilayers [8]. Several obscure theories were developed to comprehend such phenomena [9,10]. However, the complexity of hetero-structural interfaces, such as magnetic anisotropy, roughness, coupling and defect which have an obvious effect on EB,

makes it hard to target the origin of the EB in these systems [11]. Moreover, in the conventional materials with TM/TMF₂ layers [7], the positive EB was often found in magnetic materials with negative magnetization, in which the magnetization suffers a reversal from positive value to negative value below the specific temperature (compensated temperature, T_{comp}) [12–14].

In order to reveal the internal logical relation between the negative magnetization and the positive EB, a series of isomorphous crystal complexes $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{1-x}\text{Fe}^{\text{III}}_x\text{Fe}^{\text{II}}(\text{HCO}_2)_6]_n$ ($x = 0.8$ for **1**, $x = 0.7$ for **2**, $x = 0.5$ for **3**) were synthesized successfully. By adjusting the doping contents of Cr^{III} ions in this system, the magnetization reversals and EB could be controlled simultaneously. During the cooling process, the field-cooled magnetization of **1** and **2** did not increase monotonically with the temperature decreasing; instead, the magnetization of these two samples reduced to a negative value or a small positive value after arriving at the maximum, while for complex **3**, the magnetization had a dramatic increase in a similar temperature range. These results indicate that **1**, **2** and **3** belong to the *N*-, *P*-, and *Q*-type ferrimagnet, respectively, according to Néel's notation [15]. More striking, the directions of EB are highly dependent on thermo-magnetization. Complex **1** exhibits positive EB with negative magnetization, while for **2**, the negative EB behavior can be observed with positive magnetization. The origin of the H_i could be assigned to the magnetic interactions between the uncompensated spin of the host ferrimagnetic matrix and the guest antiferromagnets induced by anti-site defects of Fe^{III} and Fe^{II} ions [4]. Furthermore, we illustrate how the direction of EB is influenced by the sublattice spin configuration in the field cooling magnetization process of the host ferrimagnetic matrix.

2. Materials and Methods

All the chemical reagents for synthesis and analysis were obtained from commercial suppliers and used without further purification. The elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 C elemental analyzer. The powder X-ray diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 50 kV, 40 mA for a Cu-target tube, and a graphite monochromator. The molar ratios of Fe and Cr were determined by inductively coupled plasma (ICP, PerkinElmer Avio 500 ICP-OES). The simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at <http://www.iucr.org>. The magnetic data were collected by using the crushed crystals of the sample (**1–4**) on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T magnet. The data were corrected using Pascal's constants to calculate the diamagnetic susceptibility and an experimental correction for the sample holder was applied.

Synthesis of $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{1-x}\text{Fe}^{\text{III}}_x\text{Fe}^{\text{II}}(\text{HCO}_2)_6]_n$

$[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{0.2}\text{Fe}^{\text{III}}_{0.8}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$ (**1**): 0.25 mmol CrCl₃·6H₂O, 3 mmol FeCl₃·6H₂O and 2 mmol FeCl₂·4H₂O were dissolved in 10 mL mixture solution containing water, formate acid, and *N,N*-dimethylformamide (DMF) in a volume ratio of 0.5:1:1. The mixture was sealed in Teflon-lined stainless steel vessel, heated at 120 °C for 2 d under autogenous pressure, and then cooled to room temperature in 36 h. Black hexagonal prism-like crystals of **1** were harvested in about 20% yield based on Cr³⁺ ions. Elemental analysis (%) calcd. for **1**, C₈H₁₄Cr_{0.2}Fe_{1.8}NO₁₂ (427.12): C 22.50, H 3.30, N 3.28%; found for **1**: C 22.79, H 3.45, N 3.67%.

$[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{0.3}\text{Fe}^{\text{III}}_{0.7}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$ (**2**): The synthetic procedure of **2** is similar to that of **1**, but with 0.5 mmol CrCl₃·6H₂O, 3 mmol FeCl₃·6H₂O and 2 mmol FeCl₂·4H₂O. Black hexagonal prism-like crystals of **2** were harvested in about 20% yield based on Cr³⁺ ions. Elemental analysis (%) calcd. for **2**, C₈H₁₄Cr_{0.3}Fe_{1.7}NO₁₂ (426.73): C 22.52, H 3.31, N 3.28%; found for **2**: C 22.82, H 3.34, N 3.58%.

$[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}_{0.5}\text{Fe}^{\text{III}}_{0.5}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$ (**3**): The synthetic procedure of **3** is similar to that of **1**, but with 1 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 3 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. Black hexagonal prism-like crystals of **2** were harvested in about 20% yield based on Cr^{3+} ions. Elemental analysis (%) calcd. for **1**, $\text{C}_8\text{H}_{14}\text{Cr}_{0.5}\text{Fe}_{1.5}\text{NO}_{12}$ (426.35): C 22.56, H 3.31, N 3.29%; found for **3**: C 22.83, H 3.14, N 3.46%.

$[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$ (**4**): The block crystals of complex **4** were synthesized by solvothermal reaction. Then, 4 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 2 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 10 mL mixture solution containing water, formate acid, and *N,N*-dimethylformamide in a volume ratio of about 0.5:1:1. The mixture was sealed in a Teflon-lined stainless steel vessel, heated at 140 °C for 2 d under autogenous pressure, and then cooled to room temperature in 36 h. Rosy color hexagonal prism-like crystals of **4** were harvested in about 20% yield based on Cr^{3+} ion. Elemental analysis (%) calcd. for **4**, $\text{C}_8\text{H}_{14}\text{NCrFeO}_{12}$ (424.04): C 22.66, H 3.33, N 3.30%; found for **4**: C 22.87, H 3.13, N 3.63%.

3. Results and Discussion

3.1. Syntheses and Crystal Structures

Complexes **1–4** were all fabricated by the solvothermal reaction for two days according to our previous report [12,16]. The detailed structure analyses of these complexes are illustrated in Figure 1. The lattice parameters of **1–3** are larger than that of **4** ($[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$) [17], while smaller than that of $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$ [12]. Moreover, in complexes **1–3**, as the contents of the Fe^{III} increase, the *c* and *V* parameters increase slightly. All of this indicates that the doping of Cr^{III} into the lattice of $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$ was achieved successfully in complexes **1–3**. As shown in Figure 1a, in the unit cell of these isomorphous complexes, there are two independent metal sites occupied by divalent and trivalent metal ions, respectively. These two kinds of metal centers are both coordinated in octahedral geometry defined by six carboxylate oxygen atoms from anti, anti formate and could be served as $(4^9 \cdot 6^6)$ (yellow polyhedron in Figure 1) and $(4^{12} \cdot 6^3)$ (dark blue polyhedron in Figure 1) nodes, respectively. In **1–4**, the M–O bond lengths of $(4^9 \cdot 6^6)$ nodes are in the range of 2.1197 (17) Å–2.125 (2) Å, while the bond lengths of M–O in $(4^{12} \cdot 6^3)$ nodes range from 1.9747 (15) (Å) to 2.005 (2) (Å), which suggests that the trivalent metal (Cr^{III} and Fe^{III}) were mainly located in $(4^{12} \cdot 6^3)$ nodes and the Fe^{II} ions were in $(4^9 \cdot 6^6)$ nodes. In these networks, the $[\text{CH}_3\text{NH}_2\text{CH}_3]^+$ cations which contained the disorder N atoms were anchored into the cavities formed by metal ions and formates to balance the surplus negative charge of the network.

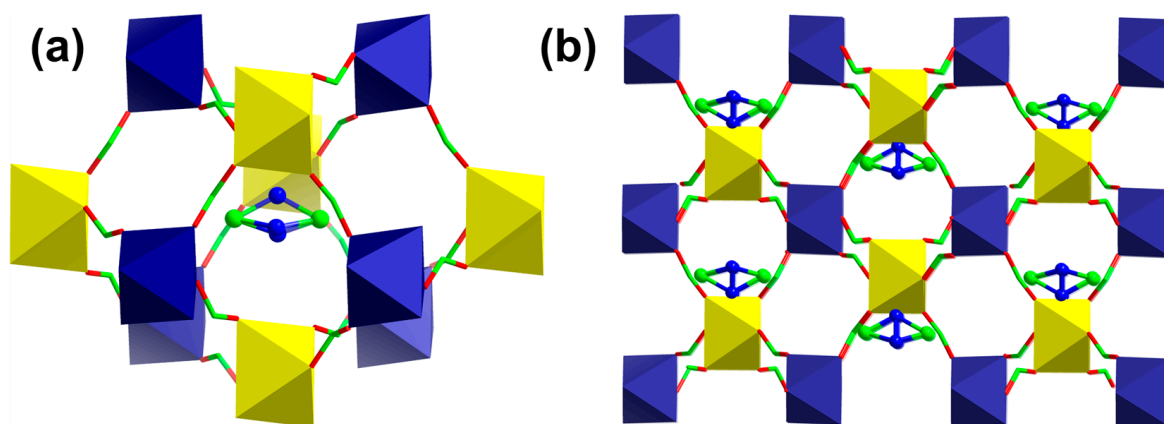


Figure 1. (a) The polyhedron view of the cavities in isomorphous complexes **1–4** constructed by $\text{M}^{\text{III}}/\text{Fe}^{\text{II}}$ ions and formates; (b) The polyhedron view of the two sublattices of M^{III} (blue) and Fe^{II} ions (yellow).

3.2. Magnetic Properties

The phase purity, metal contents, and the valence states of metal ions in **1–4** were confirmed by PXRD, ICP, and XPS, respectively (Figures S1–S3). The magnetic performances were measured by using the crystalline sample of **1–4**. As shown in Figure 2, the magnetic susceptibilities of **1–4** were measured in the range from 300 to 2 K under an applied field of 1 kOe and depicted as the plots of $\chi_m T$ vs. T and χ_m vs. T (inset in Figure 2), in which χ_m is the molar magnetic susceptibility per pair of one high spin Fe^{II} ion and one M^{III} ion. During the cooling process, the value of the $\chi_m T$ of **1–3** decreased gradually until it reached the minimum at *ca.* 37 K, which reveals the overall antiferromagnetic interactions in **1–3** (Figure 2). For **4**, during the cooling process, the $\chi_m T$ curve increases until reaching the maximum of $95.23 \text{ cm}^3 \text{ K mol}^{-1}$ at *ca.* 6.0 K. The magnetic susceptibility data above 50 K of **1–4** are fitted by the modified Curie–Weiss law $\chi_m = \chi_0 + C/(T - \theta)$ giving $\chi_0 = -0.00135 \text{ cm}^3 \text{ K mol}^{-1}$, $-0.00136 \text{ cm}^3 \text{ K mol}^{-1}$, $-0.00070 \text{ cm}^3 \text{ K mol}^{-1}$, $-0.00026 \text{ cm}^3 \text{ K mol}^{-1}$, $C = 9.09 \text{ cm}^3 \text{ K mol}^{-1}$, $8.53 \text{ cm}^3 \text{ K mol}^{-1}$, $7.41 \text{ cm}^3 \text{ K mol}^{-1}$ and $5.76 \text{ cm}^3 \text{ K mol}^{-1}$, θ value = -53.93 K , -48.35 K , -28.14 K and 4.93 K for **1–4** (Figure S4) [18]. The above results illustrate that as the doping content of Cr^{III} increased, the Curie constants of **1–4** decreased and reached the value of $5.68 \text{ cm}^3 \text{ K mol}^{-1}$ (the value expected for magnetically isolated octahedral Cr^{III} and Fe^{II} ions with spin-orbital coupling) in **4**. Moreover, the negative Weiss constants in **1–3** and positive value in **4** suggest the antiferromagnetic coupling in **1–3** and the ferromagnetic interactions in **4**. From **4** to **1**, as the doping content of Cr^{III} decreased, the Weiss constants become more negative but could not reach the value of -54.75 K in $[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCO}_2)_6]_n$. The regular change of the Curie and Weiss constants from **1** to **4** further validates the successful doping of Cr^{III} ions.

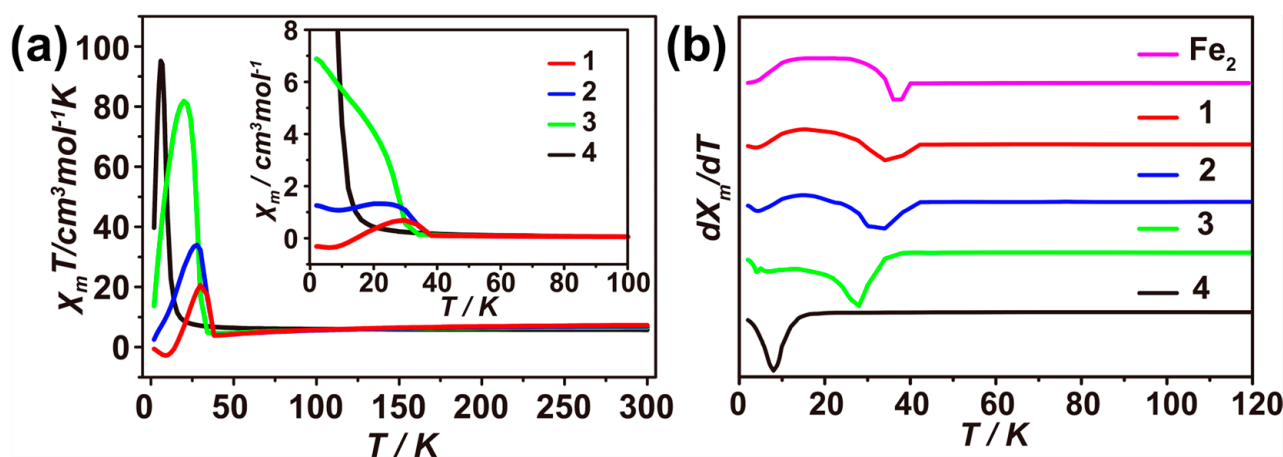


Figure 2. (a) The $\chi_m T$ vs. T plots of **1–4** per one high spin Fe^{II} ion and one M^{III} ion under applied field 1000 Oe (inset: the corresponding χ_m vs. T plots); (b) The derivative of χ_m vs. T plots of **1–4** and Fe_2 ($[\text{CH}_3\text{NH}_2\text{CH}_3]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCO}_2)_6]_n$).

Below 50 K, the χ_m plots of **1** have a similar trend with the isomorphous iron complex [12,19–21]. During the cooling process, the value of χ_m increased rapidly to the maximum of $0.68 \text{ cm}^3 \text{ mol}^{-1}$ at about 30 K and then went down and became negative at the compensation temperature (15 K). The negative value of χ_m disappeared when the applied field was larger than 3 kOe (Figure S5a). The χ_m curves of **2** reached the maximum at 23 K and decreased to the minimum at about 9 K; after that, the value of χ_m increased upon further cooling (Figure 2 and Figure S5b), which is similar to that of **1** under a larger applied field exceeding 3 kOe. The χ_m value of **3** increases monotonically as the temperature decreases (Figure 2 and Figure S5). Thus, based on the temperature

dependence of magnetization, **1**, **2**, and **3** belong to Néel's *N*-, *P*- and *Q*-type ferrimagnets, respectively [15]. Moreover, the zero field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) revealed the phase transition temperatures of **1–4** are 35 K, 33 K, 33 K, and 8 K, respectively (Figure S6). Due to the magnetic interaction between Fe^{III} and Fe^{II} being much stronger than that between Cr^{III} and Fe^{II} , as the doping contents of Cr^{III} increase, the phase-transition temperature of these complexes decreases gradually. Moreover, ZFCM also confirmed the characteristics of *N*-, *P*- and *Q*-type ferrimagnets in **1–3**. The ZFCM and FCM curves of **1** diverge at about 35 K and have a crossover at about 17 K, which is typical behavior of the *N*-type ferrimagnet. On heating, the ZFCM curve of **2** coincides with the curve of FCM at T_N . Compared to ZFCM, the FCMs of complexes **1–4** are quite different, in which the curves of **1** and **2** have a maximum value at 30 K and 23 K, respectively, suggesting the *N* and *P*-type ferrimagnetism again.

The magnetic nature and strength of magnetic interactions between $\text{Cr}^{\text{III}}\text{-Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ could be comprehended by the orbital orthogonal theory (Figure 3a) [16]. In **1–3**, the $(4^{12}\cdot 6^3)$ nodes consist of Cr^{III} and Fe^{III} ions, so ferromagnetic (between Cr^{III} and Fe^{II} ions) and antiferromagnetic interactions (between Fe^{III} and Fe^{II} ions) could be found in these complexes, leading to a ferro-ferrimagnetic state in **1–3** (Figure 3b) [22]. Thus, the spins of Fe^{III} ions in **1–3** should be antiparallel to those of ferromagnetic coupled spins of Cr^{III} and Fe^{II} . Due to the magnetic interactions between Fe^{II} and Fe^{III} being stronger than that of Fe^{II} and Cr^{III} , the total magnetization parallel to the Fe^{II} sublattice is weakened by Fe^{III} ions below T_N and enhanced by Cr^{III} ions upon further cooling. Thus, by adjusting the content of Cr^{III} ions (the values of *x*) in **1–3**, the thermal response of the magnetization could be regulated precisely.

The increase in the χ_m value with a maximum of **1** and **2** could be attributed to the fact that the spins of Fe^{II} ions are ordered firstly and parallel to the applied field at high temperatures above 35 K (T_N) [12]. After that, as the temperature decreased, the magnetization of Fe^{III} was enhanced and the total magnetization decreased upon cooling. As the temperature further decreased, the magnetization of Fe^{III} exceeded the sum of the magnetization of Cr^{III} and ordered Fe^{II} , finally leading to the negative magnetization of **1**. Compared to the Fe^{III} ions, due to the magnetization of ordered Cr^{III} ions being hard to compensate for the gap of Fe^{II} ions, **1** still exhibited negative magnetization in the range of 18 to 2 K. This indicates that restricted by the amount of the doping Cr^{III} ions, the total magnetization of Cr^{III} and Fe^{II} is still smaller than that of Fe^{III} below T_N (Néel temperature). Meanwhile, in **2**, owing to the doping content of Cr^{III} ions increased, the sum of magnetization of Cr^{III} and ordered Fe^{II} could exceed the magnetization of Fe^{III} ions below T_N ; thus, no negative magnetization can be found. The contribution of different metal ions to magnetization of **1–4** can also be seen in the plots of the first derivative of χ_m (**1–4** and Fe_2) vs. *T* (Figure 2b). In more detail, for **1** and **2**, the maximum of the derivative appears in 35–10 K, which suggests a decrease in χ_m value in the corresponding temperature range. In **3**, the χ_m plot exhibits a dramatically increasing trend in the range of 35 to 22 K, and after that, the increasing trend slows down until the temperature is below 7 K. Then, the χ_m value increases with a steep slope again during the further cooling process. The two-step increase trend of χ_m being dependent on the decreased temperature is more obvious in Figure 2b, which exhibits two valleys at about 6 K and 30 K. The first dramatic increase trend of χ_m on the cooling process could be attributed to the ferrimagnetic order of Fe^{III} and Fe^{II} spins. With further cooling below T_N , the sum of Fe^{II} magnetization in **3** exceeds that of Fe^{III} spins, and thus, the total magnetization increases constantly. In the range of 7 to 2 K, the order spins of Cr^{III} ions accelerate the raising of magnetization. In comparison, the derivative of χ_m of **4** has only one minimum at about 9 K.

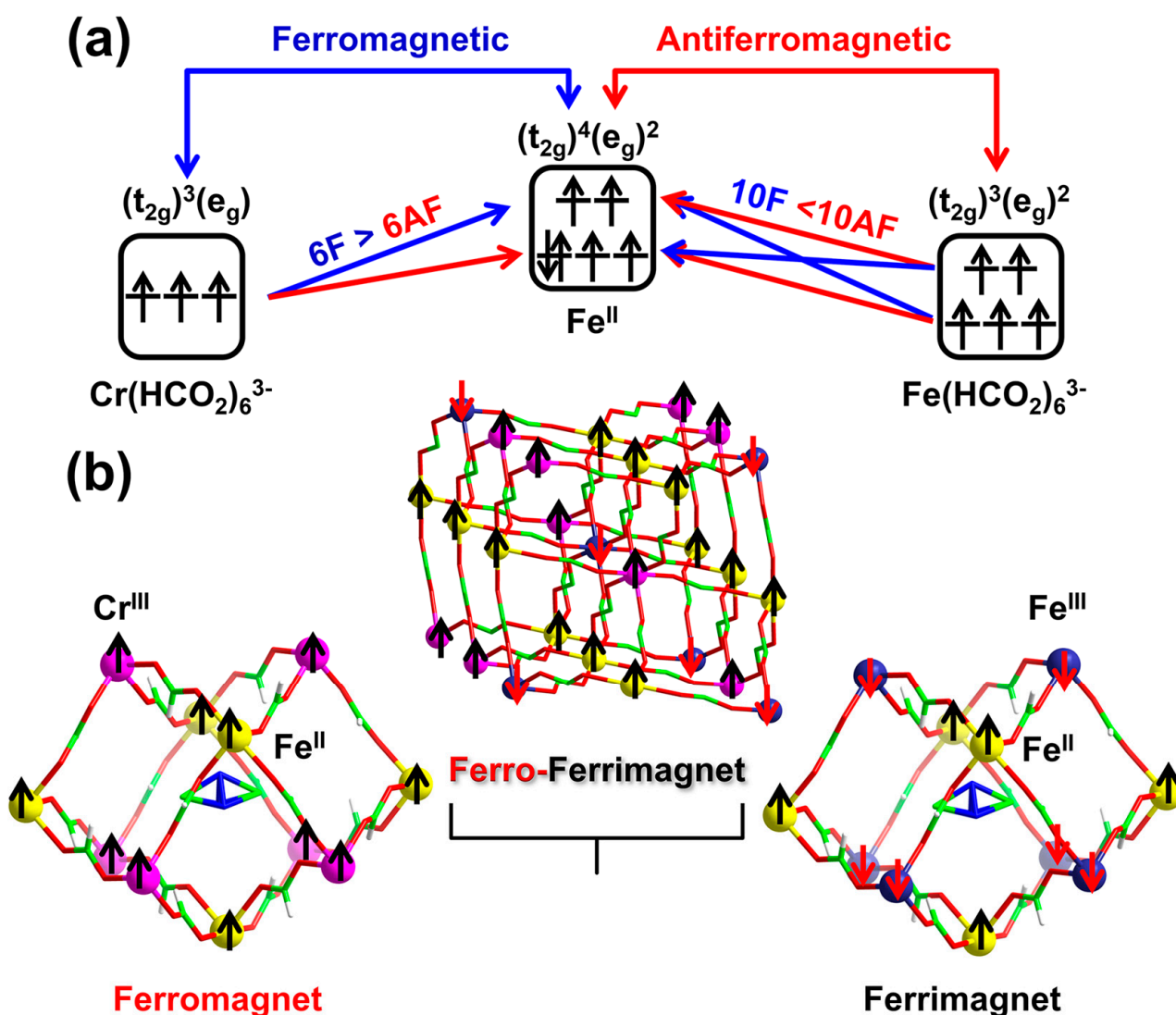


Figure 3. Schematic diagram illustrating the mixed ferro-ferrimagnetism. (a) Magnetic interactions between $\text{Cr}^{\text{III}}\text{-Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ based on orbital orthogonal theory; (b) The ferromagnetic, ferro-ferrimagnetic and ferri-magnetic state.

3.3. Exchange Bias

After that, the hysteresis loops of complexes 1–4 after the 1000 Oe field cooling process were collected in the range from -5 T to 5 T (Figure 4). Both 1 and 2 exhibit an asymmetric hysteresis loop between ± 5 T. To quantify the shift of the hysteresis loop, we define the values of shifted and average coercive fields as $H_i = (H_{C+} + H_{C-})/2$ and $H_C = (H_{C+} - H_{C-})/2$, in which H_{C+} and H_{C-} are coercivity of right-left branches. The H_i and H_C of 1 is 946 Oe and 5771 Oe under 1 kOe field cooling. Unlike that of 1, the center of the hysteresis loop of 2 shifts to the negative field with $H_i - 546$ Oe and H_C 7038 Oe. The hysteresis loop of 3 also shifts to the negative field with $H_i - 98$ Oe and H_C 6535 Oe. The hysteresis loop at 2 K after cooling in different fields of 1–3 is shown in Figure S7 and the corresponding H_i and H_C are summarized in Figure S8, in which the H_i and H_C tend to decrease slightly with the increase in the cooling field, except for the H_i of 1 under zero-field cooling. Distinct from the above three complexes, the hysteresis loop of 4 is symmetric with a coercivity of 284 Oe and saturated magnetization of about $5.9 N\beta$ at 5 T.

Since the EB effect was first observed in nanoparticles composed of an FM cobalt core and an AFM cobalt oxide shell, it usually occurs at the interface of composite FM/AFM material heterostructures. In those heterostructures, the spin of the ferromagnetic-like

component was pinned by the antiferromagnet through the field cooling process. Compared with the heterogeneous structures, the design and synthesis of single-phase bulk materials with EB effects is more challenging, due to the pinning phenomenon between different magnetic phases or multiple magnetic sublattices being hard to achieve [23]. For example, Ajaya Nayak and colleagues designed a ferrimagnetic Heusler alloy with giant tunable EB by putting ferromagnetic clusters induced by anti-site defects in the antiferromagnetic matrix [4]. In the alloy, the antiferromagnetic matrix acted as a highly anisotropic magnetic moment (μ_i) being responsible for the internal magnetic field (H_i).

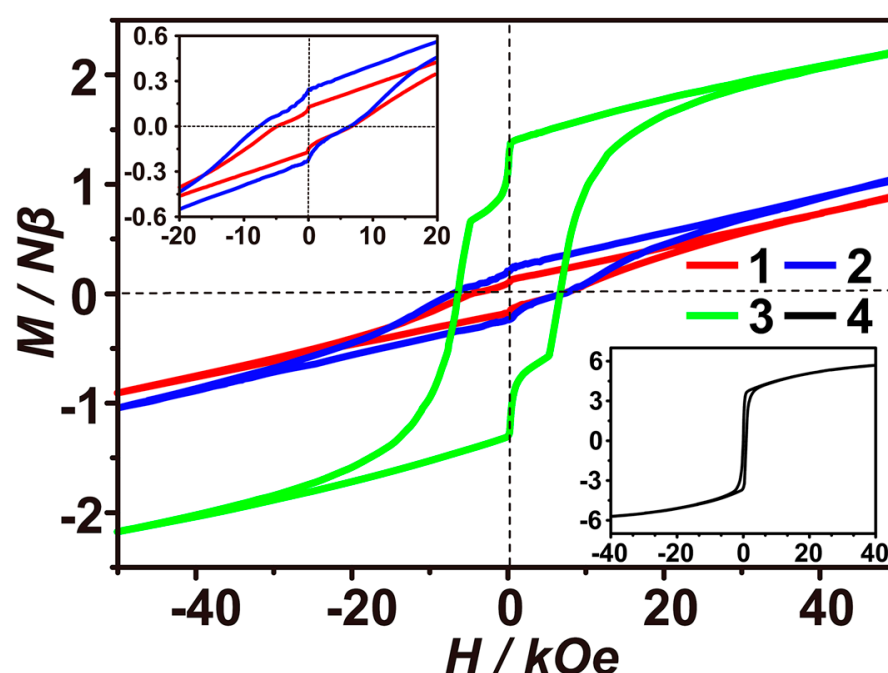


Figure 4. Plots of field-cooled hysteresis loops of 1–4 at 2 K under 1 kOe field cooling.

Distinct from the previous reports, in 1–3, the anti-site defects induce local antiferromagnetic moments embedded in the ferrimagnetic matrix. On cooling, the spin of Fe^{II} ions became ordered first, which induced the arrangement of the spins of Fe^{III} ions. More important, the spins of the guest antiferromagnetic clusters are also arranged (Figure 5a,b). The spin of the cluster is unchanged regardless of the external magnetic field. Thus, the uncompensated spins suffered antiferromagnetic interactions from the spins of the guest at low field. The coupling between the net magnetization and the guest is equivalent to providing an additional positive magnetic field (H_i). For 1, below T_{comp} with a low applied field, the uncompensated Fe^{III} lattice is antiparallel to the applied magnetic field. And the antiferromagnetic clusters act as an internal field (H_i) to transfer an antiferromagnetic coupling with Fe^{III} lattice (Figure 5b), like that of 2 and 3 (Figure 5a). However, when the external magnetic field increases, the overall magnetic moments reverse (Figure 5c), but the spins of the antiferromagnetic clusters are unchanged, and thus, the spin of the Fe^{III} lattice (uncompensated magnetic moment) suffers an additional antiferromagnetic effect, which is equivalent to adding an additional negative magnetic field to the spin of Fe^{III} lattice. Therefore, in the process of demagnetization from a positive field, a smaller magnetic field is required, and a larger magnetic field is required during the magnetization process from negative to positive fields (Figure S9 right). In 2 and 3, the magnetization (Figure 5a) of Cr^{III} and Fe^{II} are larger than that of Fe^{III} ions, and there is no pole reversal like that of 1. And the uncompensated spin suffers from antiferromagnetic coupling of the clusters, which is equivalent to adding an additional positive magnetic field to the spin of Fe^{II} lattice

(Figure S9 left). In short, the uncompensated spin in **1** and **2** experiences a force antiparallel or parallel to the applied, which provides a positive or negative H_i (Figure 5). Obvious negative exchange bias was also found in **2** under zero-field cooling, which may be caused by the pinning between the host and guest during the magnetization process (Figure S8).

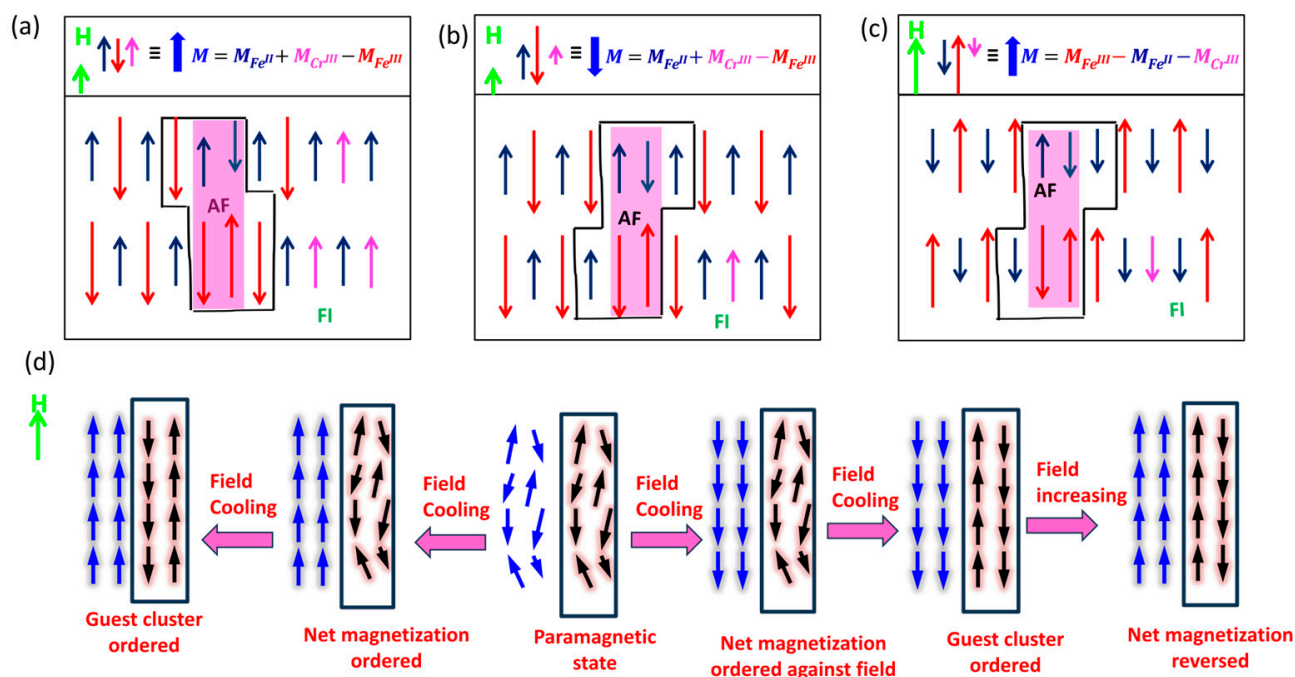


Figure 5. (a,b) Spin orientation of the host ferrimagnet and the guest antiferromagnetic cluster in *P*-/*Q*- and *N*-type ferrimagnets at low applied fields; (c) Spin orientation of that in the *N*-type ferrimagnets at high applied fields; (d) Predigested interface spin configuration of the host ferrimagnet (blue arrow) and the guest antiferromagnetic clusters (black arrow) in different conditions.

It is worth noting that the above discussion is only from a perspective of coupling; however, the magnetic anisotropy is also very important in determining the magnetic behavior of *N*-, *P*-type ferrimagnets and EB. In the EB materials, it is generally required that the ferromagnetic contribution part is ordered first. The ordered ferromagnetic induces the orientation of the antiferromagnetic part that does not flip with the external field. In this work, the anisotropy of the Fe^{II} makes it order earlier than that of the Fe^{III} during the cooling process. And as pointed out by Randy S. Fishman, the persistence of negative magnetization in small fields is caused by the spin-orbit energy cost for flipping L of Fe^{II} once it is aligned with the magnetic field [24]. Therefore, the single ion anisotropy of Fe^{II} is an important condition for non-monotonic-increased magnetization cooling and EB. And the coercivity of **2** and **3** is larger than that of **1**, which indicates that the doping of Cr^{III} improved the anisotropy of the system. And it is found that there is a step jump in the hysteresis loop at zero field in **1**–**3**, which is more pronounced in **3**. In a similar complex $[CH_3NH_2CH_3]_n[Fe^{II}(HCOO)_3]_n$, a step jump in the hysteresis loop at zero field was also found [25]. In that complex, the quantum tunneling of magnetization of the single Fe^{II} ions is responsible for this phenomenon, which is due to the magnetic phase separation caused by the competition of the super-exchange interactions conducted with the formate group and the hydrogen bonding. Meanwhile, neutron diffraction studies show that, in $[CH_3NH_2CH_3]_n[Fe^{III}Fe^{II}(HCOO)_6]_n$, in order phase, the spins of Fe^{II} ions are not completely parallel, but have a rotation angle with the *c*-axis, which indicates that the spins of Fe^{II} have canted parallel arrangements. In **1**–**3**, spin arrangements of Fe^{II} ions may also be similar to $[CH_3NH_2CH_3]_n[Fe^{III}Fe^{II}(HCOO)_6]_n$. And thus, at high fields, the

canted angles of the spins of Fe^{II} will be suppressed or enhanced by the magnetic field, depending on whether the spins are parallel or antiparallel to the external magnetic field. When demagnetizing to zero field, this angle should return to the situation without an external field, which would lead to a sharp change in the magnetic moment and a jump in the hysteresis loop at zero field.

4. Conclusions

In summary, we established an approach to design single-phase magnetic materials with controllable positive or negative EB by altering spin configuration in the field cooling magnetization process of the host ferrimagnetic matrixes. The exchange anisotropy could be attributed to the coupling effect between the guest intrinsic anti-site defects antiferromagnetic clusters and the host ferrimagnetic matrix. By controlling the content of the Cr^{III} ions, a series of ferro-ferrimagnets was realized to give *N*-, *P*- and *Q*-type ferrimagnets. Both the magnetizations of the *N*- and *P*-type ferrimagnets do not increase monotonically with temperature decreasing and exhibit the maximum at low temperatures. However, the insight mechanism of these two ferrimagnets is fundamentally different. In the *N*-type, the sublattice with smaller magnetization order is ordered quickly during the cooling process, which leads to a spin reversal at a high applied field; thus, the material exhibits the positive EB. In the *P*-type ferrimagnet, the sublattice with similar magnetization order is ordered slowly upon cooling, and thus, no spin reversals could be observed, leading to the negative EB. All these results reveal the internal logic of the negative magnetization and positive EB. Furthermore, it provided a potential way to achieve positive or negative EB magnetic materials by controlling the spin configurations of the host ferrimagnetic matrix. This work not only provides a feasible method for the design and synthesis of EB materials but also shows that the simple and direct structure design nature of the molecular-based materials can bring new possibilities for assembling specific magnetic materials and understanding their mechanism.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/magnetochemistry11020010/s1>, Table S1: Crystal data and structure refinements for 1–4; Table S2: Selected bond lengths for complexes 1–4; Figure S1: The powder X-ray diffraction (PXRD) patterns of 1–4; Figure S2: the high-resolution XPS spectra of the Cr 2p region for 1–3; Figure S3: the high-resolution XPS spectra of the Fe 2p region for 1–3; title; Figure S4: The Curie–Weiss plots of 1–4; Figures S5–S8: The magnetic measurements; Figure S9: Schematic diagram of the interface host uncompensated spin and the guest antiferromagnetic spin during the magnetization reversal with external field. See refs [26–29].

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Abbreviations

The following abbreviations are used in this manuscript:

EB	Exchange Bias
FM	Ferromagnetic
AFM	Anti-ferromagnetic
TM	Transition metal
T _{comp}	Compensated temperature
PXRD	Powder X-ray diffraction
ICP	Inductively coupled plasma
XPS	X-ray photoelectron spectroscopy
ZFCM	Zero field cooled magnetization
FCM	Field cooled magnetization

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