



# Low temperature hysteretic behavior of the interpenetrating 3-D network structured $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ magnet

Firoze Haque<sup>1</sup>, Enrique del Barco<sup>\*</sup>, Randy S. Fishman, Joel S. Miller<sup>1</sup>

Department of Physics, University Central Florida, Orlando, FL 32816-2385, USA

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6453, USA

Department of Chemistry, 315 S 1400 East, University of Utah, Salt Lake City, UT 84112-0850, USA

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## ABSTRACT

The low temperature hysteretic behavior between 40 mK and 4.8 K was obtained for the interpenetrated 3-D structured  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ . The unusual constricted hysteretic behavior reported for isomorphous  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$  was not observed, however, the  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  exhibits a single hysteresis loop and a temperature dependence of the coercivity atypical for a ferrimagnetic ordering transition. The 1.06 kOe coercive field is constant below  $\sim 0.3$  K, and shows a rapid initial decrease below 1 K, and continues decreasing at a slower rate up to at least 4.8 K. In contrast to  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$ , which has antiferromagnetic coupling of the ferrimagnetic lattices due to the reduced spin on the  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{3-}$ ,  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  exhibits ferromagnetic coupling of the ferrimagnetic lattices that dominates for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ .

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## 1. Introduction

The  $[\text{Ru}_2(\text{O}_2\text{CR})_4]^+$  cation is useful for the construction of molecule-based magnets due to it being  $S = 3/2$  and possessing two coordination sites enabling the construction of an extended network structure [1–7].  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{M}(\text{CN})_6]$  ( $M = \text{Cr}, \text{Fe}, \text{Co}$ ) possess a body centered cubic unit with two interpenetrating 3-D lattices, with each  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  bonded to two  $[\text{M}(\text{CN})_6]^{3-}$ , and each  $[\text{M}(\text{CN})_6]^{3-}$  bonded to six  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  ions, Fig. 1 [2]. The cations antiferromagnetically couple to the anions leading to ferrimagnetic ordering with a  $T_c$  as high as 33 K for  $M = \text{Cr}$ . This material exhibits anomalous (i) hysteresis, (ii) saturation magnetization, (iii) out-of-phase, imaginary AC susceptibility,  $\chi''(T)$ , and (iv) coincident zero field cooled-field (ZFC–FC) temperature-dependent magnetization data [8], and the collinear ferrimagnetic ordering is frustrated by the easy-plane anisotropy on  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  [9,10]. Furthermore,  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$  exhibits an unusual pressure dependent magnetic behavior, with  $T_c$  increasing by 83% with applied pressure, and the observed constricted hysteresis transitions from being metamagnetic-like to being ferromagnetic-like [11]. These pressure effects are reversible, and arise from the antiferromagnetic coupling between adjacent interpenetrating lattices, and the easy-plane anisotropy of the  $\text{Ru}_2$  dimer

[12] below 7 kbar [13]. Above 8 kbar the stronger antiferromagnetic coupling between sublattices and proposed spin transition on  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  leads to ferrimagnetic behavior [11,13].

This unusual hysteretic behavior, however, has not been observed for related 2- and 3-D materials, e.g., 2-D  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{M}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$  ( $M = \text{Cr}, \text{Fe}$ ) [3] or 3-D  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$  [14] or  $[\text{Ru}_2(\text{O}_2\text{CH})_4]_3[\text{Fe}(\text{CN})_6]$  [15].  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ , like  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$ , magnetically orders as a ferrimagnet, albeit with a much reduced  $T_c$  of 2.1 K, and measuring the temperature dependence of the hysteresis has been challenging due to the low  $T_c$  [2]. Herein utilizing micro-Hall effect magnetometry [16], we report magnetization hysteresis measurements on  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  in a temperature range (40 mK to 4.8 K) that extends well below the ordering temperature.

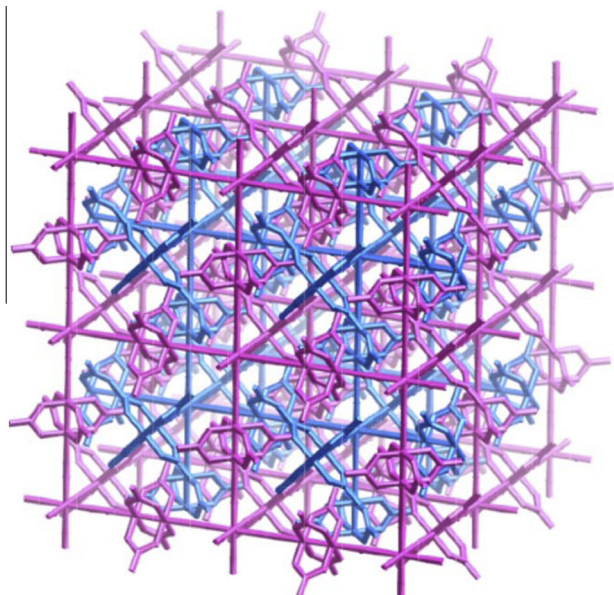
## 2. Experimental

Samples of  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  were prepared as previously reported [1,2]. Infrared spectroscopy and AC susceptibility studies were used to confirm purity on a Bruker Tensor 37 spectrometer ( $\pm 1 \text{ cm}^{-1}$ ) as KBr pellets. The magnetic data were collected on a 2-dimensional electron gas (2-DEG) micro-Hall effect magnetometer [16] by placing a polycrystalline sample of  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  next to the sensing area of the device. The Hall voltage response was then studied as a function of a magnetic field applied parallel to the sensor plane. Initially, field sweeps were taken up to 3 T applied field at 40 mK, then up to 2 T for the 150, 300, and 450 mK data. After that we collected the magnetization

<sup>\*</sup> Corresponding author. Tel.: +1 407 823 0755; fax: +1 407 823 5112.

E-mail addresses: [delbarco@physics.ucf.edu](mailto:delbarco@physics.ucf.edu) (E. del Barco), [jsmiller@chem.uta.edu](mailto:jsmiller@chem.uta.edu) (J.S. Miller).

<sup>1</sup> Tel.: +1 801 585 5455; fax: +1 801 581 8433.



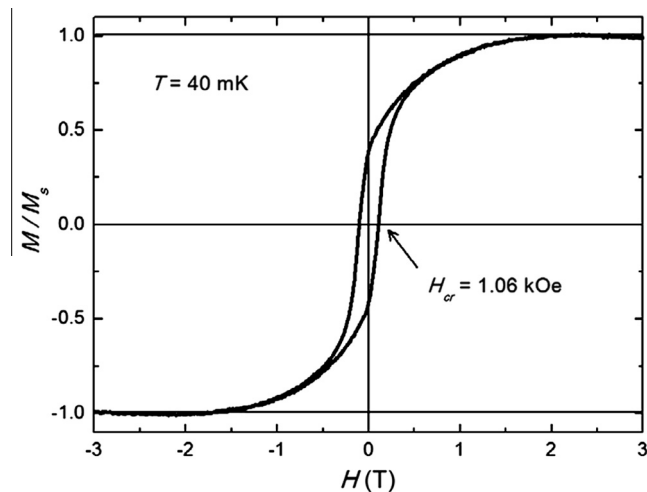
**Fig. 1.** Interpenetrating 3-D lattice (blue and magenta) structure of  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  ( $M = \text{Cr}, \text{Fe}, \text{Co}$ ) [2]. (Color online.)

hysteresis curves for a larger number of temperatures sweeping the field only up to 1 T, since the hysteretic behavior of the sample could be well resolved in that field range. The linear background data resulting from the small misalignment between the Hall sensor and the applied field were subtracted from the raw data, and the data is normalized by the saturation magnetization, which is assumed to be reached when the linear Hall response is observed above 2 T. Note that  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  is almost but not completely saturated at 3 T, as previously reported [1]. Consequently, the saturation normalization is slightly off; however, it does not interfere with the main results in this work, and allows a clearer presentation of the data.

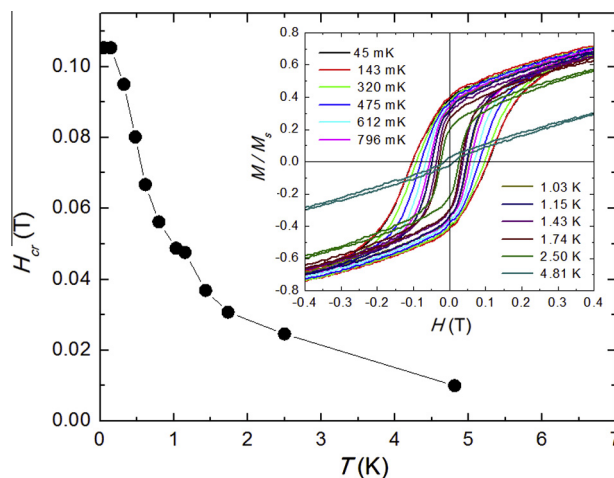
### 3. Results and discussion

The field dependent magnetization,  $M(H)$ , obtained at 40 mK and normalized to the effective saturation magnetization,  $M_s$ , is shown for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  in Fig. 2. The data shows a clear hysteretic behavior characterized by a coercive field,  $H_{cr}$ , of 1.06 kOe, which is the field necessary to reverse the magnetization of the sample, i.e.,  $H_{cr} = H(M=0)$ . Note that saturation is reached at  $\sim 2$  T applied field (lower than that previously reported [1]) as a consequence of the normalization practiced to eliminate the linear background signal, as mentioned above. The single hysteresis curve obtained for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$  (Fig. 2) differs from the anomalous constricted hysteresis reported for the isomorph complex  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$  at ambient pressure [2], for reasons not completely understood. Below, possible explanations are provided in terms of the relative strength of the dipolar energies associated to rigid and distorted sublattices, favoring ferrimagnetic ordering in the Fe-based complex.

To investigate the magnetic hysteretic behavior of  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ , field dependent measurements of the magnetization at different temperatures were performed. The inset to Fig. 3 shows the central part of the hysteresis curves ( $\pm 0.4$  T applied field) obtained at several temperatures between 40 mK and 4.8 K. A small hysteresis can be observed at the highest temperature ( $H_{cr} \sim 100$  Oe at 4.8 K), which then grows with decreasing temperature until saturating below  $\sim 150$  mK at 1.06 kOe. The temperature behavior of the coercive field is shown in the main panel



**Fig. 2.** 40 mK normalized magnetization,  $M/M_s$ , as a function of the applied magnetic field for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ .



**Fig. 3.** Temperature-dependence hysteresis and coercive field,  $H_{cr}$ , for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ . The inset shows the magnetic hysteresis loops obtained at different temperatures.

of Fig. 3. This trend of  $H_{cr}(T)$  has been previously reported for other molecule-based magnets [17]. Note that the decrease of the coercive field with temperature does not follow the typical trend associated to a magnetic ordering transition. Typically, the coercive field decreases slowly with increasing temperature, but abruptly decays in the vicinity of the transition temperature and then completely vanishes. This is the case of the ferrimagnetic ordering observed for the isomorphous  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$  previously reported [18]. For  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Fe}(\text{CN})_6]$ , the coercive field shows a drastic decrease above 150 mK, with most of the hysteresis gone at  $\sim 1.5$  K, above which its temperature dependence shows a much slower decreasing pace. This behavior could be associated to several processes, as discussed below. Indeed, similar evidence was provided from zero field cooled, field cooled (ZFC/FC) measurements [1], where a blocking temperature,  $T_b$ , of  $\sim 2$  K was interpreted as the onset for the short range ferrimagnetic ordering (due to the antiferromagnetic exchange coupling between the  $S = 3/2$   $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  and the  $S = 1/2$   $[\text{Fe}(\text{CN})_6]^{3-}$  ions), while the deviation between the ZFC and FC curves that are observed up to higher temperatures ( $\sim 4$  K) was associated with long range ordering (e.g., dipole–dipole interactions). This may also explain

the two different trends observed in the temperature dependence of the coercive field.

Note the absence of the anomalous magnetization hysteresis loops that were observed in the isomorphous  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$  [1]. The antiferromagnetic coupling between  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  and  $[\text{Cr(CN)}_6]^{3-}$  sublattices in  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$  is attributed to two effects, namely, the dipolar coupling between rigid sublattices, and the dependence of the distortion of each sublattice on their relative orientations, i.e.,  $V_{\text{Cr}}^{\text{tot}} = V_{\text{Cr}}^{\text{rig}} + V_{\text{Cr}}^{\text{dist}}$ . Assuming that each sublattice is in its classical configuration with infinite anisotropy, then the  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  spins on the  $a$ ,  $b$ , and  $c$  unit cell axes are perpendicular to those axis directions with orientations (0, 1, 1), (1, 0, 1), and (1, 1, 0), respectively. Recall that the Cr(III) spin then points along the cubic diagonal (1, 1, 1) orientation that is opposite to the total  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  spin [10]. This spin state has been experimentally confirmed by both spin muon spin relaxation measurements [19] and neutron scattering measurements [20]. The dipolar energy,  $V_{\text{Cr}}^{\text{rig}}$ , for two rigid sublattice spin states oriented ferromagnetically is

$$V_{\text{Cr}}^{\text{rig}} = S_{\text{Ru}}^2 K_1 + S_{\text{Ru}} S_{\text{Cr}} K_2 \quad (1)$$

where  $K_1$  is the coupling between the  $S_{\text{Ru}} = 3/2$   $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  ions, and  $K_2$  is the coupling between  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$  and  $S_{\text{Cr}} = 3/2$  Cr(III) ions. Note that the coupling between the Cr(III) spins vanishes by symmetry. By performing the dipolar sum, which only depend on the spin orientations,  $K_1 = -4.03 \times 10^{-3}$  meV, and  $K_2 = 9.47 \times 10^{-4}$  meV. Hence, the Ru ··· Ru interaction favors ferromagnetic alignment of the two sublattices while the Ru ··· Cr interaction favors antiferromagnetic alignment. Because  $|K_1| > |K_2|$ , the Ru ··· Ru interaction dominates and the net dipolar interaction between rigid sublattices is ferromagnetic. With spin  $M_{\text{sl}} = 1.9$  for each sublattice, the antiferromagnetic coupling  $V_{\text{Cr}}^{\text{tot}} = M_{\text{sl}}^2 K_{\text{tot}} = 1.88 \times 10^{-2}$  meV is experimentally observed. This value should be compared to the theoretical result of  $V_{\text{Cr}}^{\text{rig}} = -6.94 \times 10^{-3}$  meV, which has the opposite sign and favors ferromagnetic alignment of the two sublattices. Hence, the dependence on the sublattice distortion with respect to the relative spin orientation of the two sublattices  $V_{\text{Cr}}^{\text{dist}}$  must favor antiferromagnetic alignment. This distortion term includes quantum corrections to the spin state, which may also depend on the relative orientations of the two sublattices and which are indicated by recent neutron-scattering measurements [20].

For  $S_{\text{Fe}} = 1/2$   $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Fe(CN)}_6]$  the ground state of each sublattice conjectured to be identical to  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$ . Again, the net interaction between sublattices will have two contributions, i.e.,  $V_{\text{Fe}}^{\text{tot}} = V_{\text{Fe}}^{\text{rig}} + V_{\text{Fe}}^{\text{dist}}$ . For  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Fe(CN)}_6]$ , however, the dipolar interaction between rigid sublattices oriented ferromagnetically is given by

$$V_{\text{Fe}}^{\text{rig}} = S_{\text{Ru}}^2 K_1 + S_{\text{Ru}} S_{\text{Fe}} K_2. \quad (2)$$

The dipolar sums  $K_1$  and  $K_2$  in Eq. (2) only depend on the spin orientations, and are the same as for the Cr compound. But due to the reduced Fe(III) spin,  $V_{\text{Fe}}^{\text{rig}} < V_{\text{Cr}}^{\text{rig}}$ , and the Ru ··· Ru interaction favoring ferromagnetic alignment is even more dominant. Hence, ferromagnetic alignment of the two sublattices is more strongly favored than for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$ . The net coupling between sublattice, of course, must also include the effect of the sublattice distortion,  $V_{\text{Fe}}^{\text{dis}}$ . However, the argument above implies that the Ru ··· Ru interaction, favoring  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$  alignment, is more important in  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Fe(CN)}_6]$  than for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$ . Consequently, the sublattice distortion energy,  $V_{\text{Fe}}^{\text{dist}}$ , may not be sufficiently large to produce antiferromagnetic alignment of the sublattices as occurs for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$ .

However, one other issue arising from the low transition temperature extracted from the maximum in the ZFC magnetization

is the observation of hysteresis at much higher temperatures, at least up to 4.8 K as reported in this work. As mentioned before, this may be reminiscent of a transition between short-range ordering (exchange-type) to long-range order (dipolar type), as hinted from the reported behavior of the ZFC–FC magnetizations [1]. Dipolar ordering is also proportional to the spin value of the interacting units [21]. Therefore, if present for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Fe(CN)}_6]$ , it should appear at lower temperatures than for  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$ , where the net spin per unit cell is higher. Although it may also be present in the latter, perhaps still at temperatures below the short-range ordering, in the former may become relevant since it acts above the short-range ordering temperature.

#### 4. Conclusion

$[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Fe(CN)}_6]$  is isostructural to  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3\text{[Cr(CN)}_6]$ , but exhibits a different temperature dependent hysteretic behavior and a metamagnetic-like phase is not observed. The atypical temperature behavior of the coercive field, with two distinct regimes, may be associated to a transition from short to long-range dipolar ordering, as evidenced in the ZFC–FC data. To verify that the total coupling in the Fe compound is ferromagnetic, we hope to evaluate the effect of sublattice distortion  $V^{\text{dist}}$  on both the Fe and Cr compounds in the future. If the model proposed in this paper is correct, then the sublattice state in the Fe compound is more “rigid” and less easily distorted than the sublattice state of the Cr compound. Consequently, the ferromagnetic interaction between rigid sublattices due to the dipolar interaction dominates. We hope that future theoretical work can verify this conjecture.

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