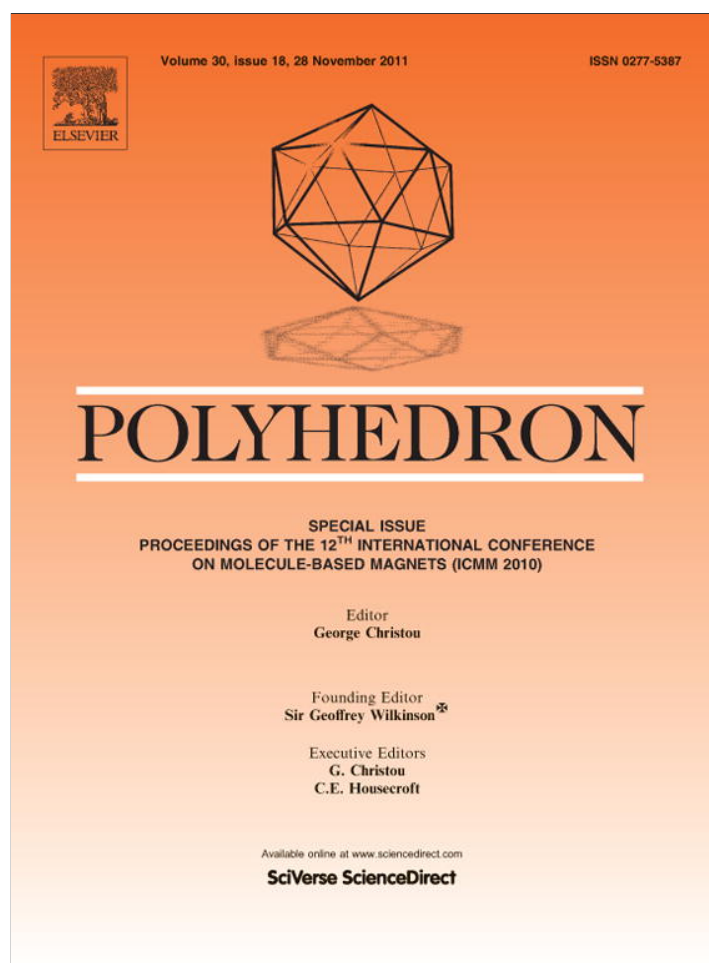


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## Metamagnetic phase transition in a diruthenium compound with interpenetrating sublattices

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## ABSTRACT

The diruthenium compound  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$  may be the only known material that contains two weakly-coupled, magnetically-ordered sublattices occupying the same three-dimensional volume. Due to the strong easy-plane anisotropy on each  $\text{Ru}_2$  complex, the moment of each sublattice is constrained to one of the eight cubic diagonals. At low fields, the two sublattices are antiferromagnetically aligned by weak dipolar and deformation energies. But above a metamagnetic critical field of about 1000 Oe, the sublattice moments become ferromagnetically aligned and the net magnetization increases dramatically. We have successfully modeled this metamagnetic transition by assuming that the individual sublattice spin configurations are only weakly distorted by the magnetic field. This model suggests that the ground state of each sublattice undergoes a phase transition at a pressure of about 7 kbar. The drop in the sublattice moment and the rise in the sublattice susceptibility above 7 kbar can be explained by a high- to low-spin transition ( $S = 3/2$  to  $1/2$ ) on the mixed-valent diruthenium complexes.

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Diruthenium tetracarboxylate,  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$  (Me = methyl,  $\text{CH}_3$ ) [1–4], or  $\text{Cr}(\text{Ru}_2)_3$  for short contains two weakly-interacting, magnetic sublattices that occupy the same three-dimensional volume. At low fields, the two sublattices are antiferromagnetically (AF) coupled by the weak exchange interaction  $K_c \sim 5 \times 10^{-3}$  meV, which is much smaller than the exchange interaction  $J_c \sim 1.5$  meV between neighboring Cr and  $\text{Ru}_2$  moments on the same sublattice. Due to this weak AF coupling, the two sublattices become aligned [5] above a small metamagnetic critical field  $H_c \sim K_c/\mu_B \approx 1000$  Oe. Plots of the field-dependent average magnetization  $2\mu_B M_{av}(T, H)$  for a polycrystalline sample at ambient pressure are given in Fig. 1.

We have successfully modeled the metamagnetic transition in this compound by assuming that the sublattice ground states are only weakly perturbed by the magnetic field [6,7]. The net spin  $M_{si}\mathbf{n}_i$  ( $i = 1$  or  $2$ ) of each sublattice is then confined by anisotropy to one of the eight cubic diagonals ( $h, k, l$ ) with  $h, k$  and  $l = \pm 1$ . With increasing field, the sublattice orientations  $\mathbf{n}_i$  shift from one cubic diagonal to another until they are aligned as close as possible to the external magnetic field  $H\mathbf{m}$ . A schematic of the sublattice spins is shown in the inset to Fig. 1.

A single sublattice of  $\text{Cr}(\text{Ru}_2)_3$  contains Cr(III) ions at the corners of the cubic unit cell and mixed-valent (II/III)  $\text{Ru}_2$  complexes [1] at the midpoints of each edge. Using mean-field theory to approximate

the exchange interaction between neighboring  $S = 3/2$  Cr and  $\text{Ru}_2$  complexes within each sublattice, we constructed the ground state in Fig. 2. Due to the “paddle-wheel” molecular environment produced by the surrounding four Me groups, each  $\text{Ru}_2$  spin  $\mathbf{S}$  experiences the easy-plane anisotropy  $D(\mathbf{S} \cdot \mathbf{v})^2$  with  $D \approx 100$  K or 8.6 meV [8,9] (the unit vector  $\mathbf{v}$  points to one of the neighboring Cr ions).

Each unit cell contains three distinct  $\text{Ru}_2$  sites  $a, b$ , and  $c$  along the  $x, y$ , and  $z$  axis, respectively. The total  $\text{Ru}_2$  spin of the  $a, b$ , and  $c$  sites lies along one cubic diagonal and the Cr spin lies opposite. The net sublattice spin  $M_{si}\mathbf{n}$  points opposite the Cr spin.

For classical spins and infinite anisotropy, the  $\text{Ru}_2$  spins on the  $a, b$ , and  $c$  sites will lie in the  $yz, xz$ , and  $xy$  planes, as shown in Fig. 2. The total sublattice spin at  $T=0$  is then given by  $M_{si}(0) = (\sqrt{6} - 1)S \approx 2.17$  per  $\text{Cr}(\text{Ru}_2)_3$  unit cell. But for finite anisotropy and quantum spins, the  $\text{Ru}_2$  spins will cant out of the easy planes towards the (111) direction, albeit with suppressed amplitudes.

The body-centered cubic compound  $\text{Cr}(\text{Ru}_2)_3$  contains two cubic sublattices, with the Cr ions of one sublattice sitting at the centers of the unit cells of the other. The weak AF coupling  $K_c$  between the two sublattices contains two contributions. The dipolar interaction between non-distorted magnetic sublattices is ferromagnetic (FM) with an amplitude of about  $1 \times 10^{-3}$  meV. But the distortion of the two sublattices due to their dipolar interaction depends on their relative orientations. We recently discovered [10] that the distortion energy has a larger magnitude when the

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sublattices are AF aligned. This distortion energy must be sufficiently negative to produce the net AF exchange interaction  $K_c \approx 5 \times 10^{-3}$  meV.

A two-dimensional  $\text{Cr}(\text{Ru}_2)_3$  compound has also been synthesized [3]. Due to the reduced coordination of the  $\text{Ru}_2$  complexes that protrude above and below each plane, this compound is less magnetically frustrated than three-dimensional  $\text{Cr}(\text{Ru}_2)_3$  and a collinear spin state is possible [11].

Because  $K_c \ll J_c$ , the metamagnetic transition in three-dimensional  $\text{Cr}(\text{Ru}_2)_3$  can be described by a very simple model. For a fixed orientation  $\mathbf{n}$ , the spin configuration of each sublattice is only weakly perturbed by a field of order  $H_c \sim K_c/\mu_B$ , which is much smaller than the internal exchange field  $J_c/\mu_B$ . Therefore, the sublattice magnetization responds linearly to an external magnetic field.

The total susceptibility due to the distortion of the sublattice ground states (with zero-field moments along the  $\mathbf{n}_1$  and  $\mathbf{n}_2$  directions) in a magnetic field  $H\mathbf{m}$  can be written as [10]

$$\begin{aligned} \chi_{dis}(\mathbf{n}_1, \mathbf{n}_2; \mathbf{m}) = & 2\chi_0(1 - \mathbf{n}_1 \cdot \mathbf{n}_2) + 2\chi_1 \\ & + \chi_2 \{ \sin^2 \theta_1 + \sin^2 \theta_2 \} \\ & + \chi_3 \{ \sin^4 \theta_1 + \sin^4 \theta_2 \}, \end{aligned} \quad (1)$$

where  $\cos \theta_i = \mathbf{n}_i \cdot \mathbf{m}$ . Notice that  $\chi_{dis}$  has been expanded in even Legendre polynomials  $P_l(\cos \theta_i)$  up to  $l = 4$ . Odd Legendre polynomials are not included in this expansion in deference to the Onsager relation [12], which states that the diagonal components of the susceptibility tensor must be even with respect to reversing the direction of the magnetic field ( $\theta_i \rightarrow \pi - \theta_i$ ).

The first term in Eq. (1) reflects the dependence of the sublattice distortion on the relative orientation of the two sublattices. For  $\chi_0 > 0$ , the sublattices are more distorted when AF aligned; for  $\chi_0 < 0$ , the sublattices are more distorted when FM aligned. All susceptibility parameters  $\chi_n$  are subject to the constraint that  $\chi_{dis}(\mathbf{n}_1, \mathbf{n}_2; \mathbf{m}) > 0$  for all  $\mathbf{n}_1$  and  $\mathbf{n}_2$ .

For each cluster containing  $N_{Cr}$   $\text{Cr}(\text{Ru}_2)_3$  unit cells with sublattice orientations  $\mathbf{n}_1$  and  $\mathbf{n}_2$ , the total magnetization is given by

$$\begin{aligned} 2\mu_B \mathbf{M}_{clust}(\mathbf{n}_1, \mathbf{n}_2; \mathbf{m}) = & \mu_B M_{sl} N_{Cr} (\mathbf{n}_1 + \mathbf{n}_2) \\ & + \frac{N_{Cr}}{2} H \mathbf{m} \chi_{dis}(\mathbf{n}_1, \mathbf{n}_2; \mathbf{m}). \end{aligned} \quad (2)$$

Due to thermal fluctuations out of the ordered ground state, the size  $N_{Cr}$  of the magnetically-correlated clusters grows with increasing temperature.

Therefore, the total energy of a magnetic configuration with sublattice orientations  $\{\mathbf{n}_{1i}, \mathbf{n}_{2i}\}$  on cluster  $i$  in a magnetic field  $H\mathbf{m}$  is

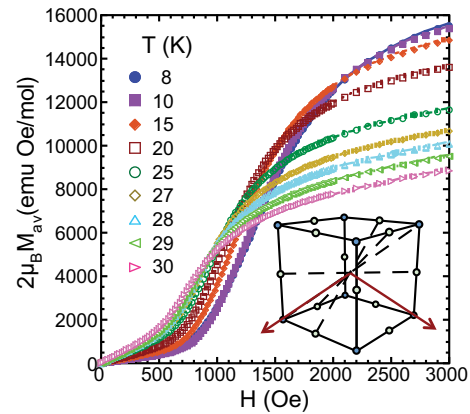
$$\begin{aligned} E = & N_{Cr} \\ & \times \sum_i \left\{ -\mu_B M_{sl} (\mathbf{n}_{1i} + \mathbf{n}_{2i}) \cdot \mathbf{H} + K_c M_{sl}^2 \mathbf{n}_{1i} \cdot \mathbf{n}_{2i} - \frac{H^2}{4} \chi_{dis}(\mathbf{n}_{1i}, \mathbf{n}_{2i}; \mathbf{m}) \right\}. \end{aligned} \quad (3)$$

For a polycrystalline sample, the magnetization must be averaged over all field directions  $\mathbf{m}$ . Hence, the average magnetization

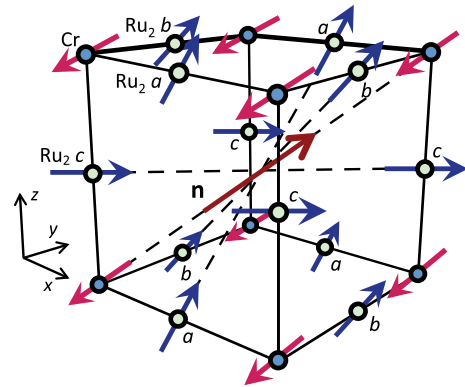
$$2\mu_B M_{av} = 2\mu_B \sum_i \int \frac{d\Omega}{4\pi} \langle \mathbf{M}_{clust}(\mathbf{n}_{1i}, \mathbf{n}_{2i}; \mathbf{m}) \rangle \cdot \mathbf{m} \quad (4)$$

contains both an integral over all orientations of the external field and a thermal average over the  $8 \times 8 = 64$  possible values for  $\{\mathbf{n}_{1i}, \mathbf{n}_{2i}\}$  within each cluster.

Notice that  $M_{av}(T, H)$  contains seven parameters: the four components of the sublattice susceptibility  $\chi_n$ , the sublattice spin  $M_{sl}$ , the weak AF interaction  $K_c$  between sublattices, and the num-



**Fig. 1.** Experimental data (points) and fits (curves) for the average magnetization of a polycrystalline sample at ambient pressure. Data taken from Ref. [5]. The inset shows possible orientations for the sublattice spins, restricted to the cubic diagonals. Cr ions are at the corners of each unit cell;  $\text{Ru}_2$  complexes at the midpoints of each edge.



**Fig. 2.** The predicted ground state of a single sublattice of  $\text{Cr}(\text{Ru}_2)_3$  for infinite anisotropy and classical spins. The net sublattice spin points along  $\mathbf{n}$ , given by the (111) vector at the center of the cube.

ber  $N_{Cr}$  of  $\text{Cr}(\text{Ru}_2)_3$  unit cells within each cluster. Due to the assumption of a nearly-rigid sublattice spin state, the AF interaction  $J_c$  within each sublattice only enters the energy and average magnetization implicitly through the sublattice spin  $M_{sl}$ , which vanishes above  $T_c \propto S^2 J_c$ . Neglecting the sublattice susceptibility, the average value for the saturation magnetization would be  $2\sqrt{3}\mu_B M_{sl}$ .

Fits based on this model break down close to  $T_c \approx 33$  K and at high fields because the field-induced change in each sublattice spin becomes a substantial fraction of the zero-field spin  $M_{sl}$ . So the assumption of a nearly rigid sublattice ground state breaks down at high fields and near  $T_c$ . We have employed a field cutoff of 3000 Oe and a maximum temperature of 30 K.

Results for the fits at ambient pressure are shown in Fig. 1. The interaction between sublattices  $K_c$  is about  $5.2 \times 10^{-3}$  at low temperatures and increases to about  $7.5 \times 10^{-3}$  meV at 30 K. As expected, the sublattice spin  $M_{sl}(T)$  decreases with temperature and has a low-temperature value of about 1.9. Due to the behavior of quantum spins with finite anisotropy, this is smaller than the classical result with infinite anisotropy  $M_{sl}(0) \approx 2.17$ . The fitting results presented in Fig. 1 are slightly different from those presented in Ref.[6] because the sublattice susceptibility  $\chi_{dis}(\mathbf{n}_1, \mathbf{n}_2; \mathbf{m})$  used in our earlier work contained odd Legendre polynomials and thereby violated Onsager's relation [12].

We find that  $N_{Cr}$  grows very rapidly with increasing temperature and scales roughly as  $(1 - T/T_c)^{-3\nu}$  with a critical exponent  $\nu = 1.05$ . The ability to estimate critical exponents directly from magnetization data is highly unusual: in all other cases known to us, critical exponents can only be estimated from elastic neutron-scattering measurements or from internal probes like NMR, Mössbauer spectroscopy, or muon spin rotation.

At ambient pressure, the susceptibility is dominated by a positive  $\chi_0$  term, which implies that the sublattices are most distorted when AF aligned and explains why the sublattices are AF coupled in zero field. The increase of  $\chi_0$  with temperature may explain the similar temperature dependence of  $K_c$ .

This model has also been used to understand the effect of pressure [13] on  $Cr(Ru_2)_3$ . Above about 7 kbar, the sublattice spin  $M_{sl}$  drops by roughly 50% and the susceptibility components  $\chi_n$  with  $n \geq 1$  grow dramatically. Both the drop in  $M_{sl}$  and the reduced rigidity of each sublattice provide indirect evidence for a high- to low-spin transition ( $S = 3/2$  to  $1/2$ ) on the  $Ru_2$  complexes.

Since the different orbital configurations of the  $Ru_2$  core have nearly the same energy [14], it is not surprising that both low-spin [15] and spin-admixed [16] diruthenium compounds have been previously synthesized. But  $Cr(Ru_2)_3$  would provide the first example of a pressure-induced high- to low-spin transition for a diruthenium compound.

Clearly, a remarkable amount of information can be extracted from the magnetization of a polycrystalline sample. A careful analysis of the average magnetization of a polycrystalline sample provides important information about the magnetic ground state, exchange interactions, and magnetic correlations. We are hopeful that neutron-scattering measurements on a deuterated polycrystalline sample will provide confirmation of the dominant anisotropy axis and of the critical exponent  $\nu$ .

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