Giant Antiferromagnetically Coupled Moments in a Molecule-Based Magnet with Interpenetrating Lattices

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The molecule-based magnet [Ru₂(O₂CMe)₄]₃[Cr(CN)₆] contains two weakly-coupled, interpenetrating sublattices in a body-centerd cubic structure. Although the field-dependent magnetization indicates a metamagnetic transition from an antiferromagnet to a paramagnet, the hysteresis loop also exhibits a substantial magnetic remanence and coercive field uncharacteristic of a typical metamagnet. We demonstrate that this material behaves like two giant moments with a weak antiferromagnetic coupling and a large energy barrier between the orientations of each moment. Because the sublattice moments only weakly depend on field in the transition region, the magnetic correlation length can be directly estimated from the magnetization.

Due to the importance of weak interactions that are commonly neglected in solid-state materials, molecule-based magnets exhibit a variety of novel behavior. One of the most fascinating and puzzling molecule-based magnets containing two interpenetrating lattices of [Ru₂(O₂CMe)₄]₃[Cr(CN)₆] (Me = methyl, CH₃) exhibits an unusual “wasp-waisted” hysteresis loop that is attributed to the weak antiferromagnetic (AF) coupling between its two sublattices. The shape of the initial M(H) data plotted in Fig.1, with a shallow slope followed by a rapid rise, is commonly associated with a metamagnetic transition between AF and paramagnetic (PM) states, which has been observed both in solid-state systems like FeCl₂ and DyAl garnet as well as in several other molecule-based magnets. However, typical metamagnets do not exhibit the nonzero remanent magnetization and coercive field found in the hysteresis loop of Cr(Ru₂)₃ compounds with interpenetrating lattices.

We argue that a Cr(Ru₂)₃ compound with interpenetrating lattices behaves like two macroscopic AF coupled moments with a large energy barrier between the orientations of each moment. Quasi-one- or two-dimensional materials that magnetically order in three dimensions due to a weak coupling between sublattices are fairly common, even among molecule-based magnets. Much rarer are materials where each of the weakly-interacting sublattices is fully ordered in three dimensions.

A single lattice of Cr(Ru₂)₃ is sketched in the inset to Fig.1, where every pair of Ru ions bridges two [Cr(CN)₆]³⁻ ions located at the corners of the cubic unit cell and separated by a1 = 13.4 Å. While each Cr(III) ion has a spin S = 3/2, each Ru₂ dimer is in a II/III mixed-valence state with a total spin S = 3/2. Due to the “paddle-wheel” molecular environment produced by the surrounding four Me groups, each Ru₂ moment experiences a strong easy-plane anisotropy with D ≈ 100 K or 8.6 meV. The easy plane lies perpendicular to the axis joining the Ru₂ sites with the neighboring Cr ions. Although a single-lattice Cr(Ru₂)₃ compound has been synthesized, the resulting samples are amorphous. A Cr(Ru₂)₃ compound with interpenetrating lattices contains a second identical lattice inserted through the open space of the first lattice resulting in a body-centered cubic structure.

Most of the properties of the interpenetrating-lattice compound can be explained by a simple model with strong easy-plane anisotropy D on the Ru₂ sites, AF intra-sublattice exchange Jₚ between neighboring Cr and Ru₂ sites on each sublattice, and a weak AF inter-sublattice exchange Kₚ between moments on the two sublattices. The coupling Kₚ is the sum of the dipolar energy and the superexchange interaction through weakly-overlapping molecular orbitals on the two sublattices.

The key to understanding Cr(Ru₂)₃ with interpenetrating lattices is to construct the correct ground state for the single-lattice compound. Each Ru₂ spin pair in Fig.1
is labeled as $a$ (along the $x$ axis), $b$ (along $y$), or $c$ (along $z$). In the classical limit with infinite anisotropy, the $a$, $b$, or $c$ spins must lie in the $yz$, $xz$, or $xy$ planes, respectively. In the quantum case, the Ru$_2$ spins will have small, but nonzero components in the classically-forbidden directions. For both classical and quantum spins, AF order is frustrated by the easy-plane anisotropy. A similar situation arises in cubic pyrochlores like Ho$_2$Ti$_2$O$_7$, where ferromagnetic order is frustrated by local [111] anisotropy [10].

Both classical and quantum calculations provide the same magnetic ground state. The sum of the Ru$_2$ $a$, $b$, and $c$ spins points opposite to the Cr spin along one of the four diagonals of the cube. Accounting for the two orientations of the moment along each diagonal, there are eight domains in zero field. For classical spins with infinite anisotropy, the net moment along one of the diagonals is $M_{sl} = (\sqrt{6} - 1) S \approx 1.45 S$ per Cr ion. In both classical and quantum calculations, the Ru$_2$ spins approach the cubic diagonal as $D/J_c$ is reduced. The quantum result $M_{sl} \approx 1.21 S$ for the single-lattice moment with $D/J_c = 5$ is lower than the classical result because the expectation values of the Ru$_2$ spins are reduced in magnitude from 1.5 to about 1.23.

Based on quantum mean-field calculations with $D/J_c = 5$ and $J_c = 1.72$ meV (see below), the single-lattice compound experiences a spin-flop transition at $H_{sf} \approx 2.78 J_c \mu_B \approx 80$ T with the field along one of the cubic diagonals. Above $H_{sf}$, the Cr and total Ru$_2$ moments cant away from the cubic diagonal and, until all the moments become aligned ferromagnetically (FM) at an even higher field, the magnetization $2 \mu_B M$ is no longer parallel to $H$.

Now consider Cr(Ru$_2$)$_3$ with interpenetrating lattices. Assuming that $K_c \ll J_c$ and $\mu_B H \ll J_c S$, the sublattice moments $M_{sl} \mathbf{n}_j$ ($j = 1$ or 2) are rigid with the same spin configuration as in the inset to Fig.1 but pointing along arbitrary cubic diagonals. Thermal equilibrium between the 64 possible configurations $\{\mathbf{n}_1, \mathbf{n}_2\}$ is established within correlated clusters of size $\xi$. The stable phases are shown in Fig.2 along with the fraction of configurations I, II, and III when averaged over all field directions $\mathbf{m}$. Notice that the AF configuration vanishes only with the appearance of the PM state. In zero field, $M_{sat}$ obeys the simple functional form $M_{sat}/M_{sat} = 1 - (H_c/H)^2$ plotted in Fig.2(a).

We must modify Eq. (1) to account for the small distortion of the single-lattice ground state with field. That distortion is responsible for the small linear susceptibility observed within the AF state at low temperature and small fields, and for the even smaller differential susceptibility $2 \mu_B dM/dH$ observed within the PM state at high fields. For classical spins and large anisotropy, the magnetic ground state with $\mathbf{n}_j = \mathbf{m}$ cannot be deformed until very large fields, when the Cr spins tilt away from the $-\mathbf{m}$ direction. But for $\mathbf{n}_j = -\mathbf{m}$, the Ru$_2$ spins can easily cant towards the field direction.

So the simplest form for the susceptibility of sublattice $j$ is $\chi_j = \chi_{sl} \sin^2(\theta_j/2)$ where $\theta_j = \cos^{-1}(\mathbf{n}_j \cdot \mathbf{m})$ is the angle between the field and moment directions. Hence, $\chi_j = 0$ when $\theta_j = 0$ and $\chi_j = \chi_{sl}$ when $\theta_j = \pi$. The non-interacting susceptibility of the magnetic configura-

![FIG. 2: (a) The $T = 0$ average moment and non-interacting linear susceptibility $\chi_{nint} H/2$ and (b) the fractions of the AF state and configurations I, II, and III versus $\mu_B H/K_s S$ assuming classical spins and large anisotropy.](image)
The magnetization by averaging over field directions. For the critical exponent. Since the functional form 

\[ \xi(T) \propto [(T_c - T)/T_c]^{-\nu} \]

is only expected close to \( T_c \), it is remarkable that this form is only apparent at 10 K. Other evidence for the mean-field nature of the phase transition in \( \text{Cr}(Ru) \) comes from the magnetization of the single-lattice compound [4], which although amorphous closely follows a Brillouin function and vanishes near \( T_c \) like \((T_c - T)^{1/2}\).

The “saturation” magnetization \( 2\mu_B M_{\text{sat}}(T) = \sqrt{\xi(T)} \) per Cr atom plotted in Fig. 3(a) gives the average magnetization when the two non-distorted sublattice moments are aligned. Nevertheless, the magnetization continues to rise with increasing field due to the deformation of the ferrimagnetic ground state of each sublattice. Indeed, Vos et al. [4] found that the magnetization at 5 K rises from 16.937 emu Oe/mol at 0.5 T to 20,800 emu Oe/mol at 5 T, far above the “saturation” value of 17,286 emu Oe/mol. In rough agreement with the assumed form for the non-interacting susceptibility \( \chi_{\text{int}} \), the high-field differential susceptibility of 0.086 emu/mol is about nine times smaller than the low-field linear susceptibility of 0.81 emu/mol. Notice that the 30 K clusters with \( N_{\text{Cr}} = 6464 \) have correlation lengths \( \xi \approx 15 \text{Å} \) and sublattice magnetizations \( \mu_B N_{\text{Cr}} M_{\text{sat}}(T = 30 \text{K}) \approx 4500 \mu_B \).

At \( T = 5 \) K, the saturation magnetization is significantly lower than the classical result with \( D = \infty \). But the single-lattice moment \( M_{\text{sl}} \) for quantum spins decreases rapidly with increasing \( D/J_c \) from its maximal value of \( 2S \) per Cr ion when \( D = 0 \). The fitted saturation value can be used to estimate that \( D/J_c \approx 5 \) and \( J_c \approx 1.72 \text{meV} \). Another estimate for \( J_c \) comes from the mean-field result \( T_c \approx 4.05J_c = 33 \) K for the transition temperature with \( D/J_c = 5 \), yielding the smaller value \( J_c \approx 0.70 \text{meV} \). However, mean-field theory typically overestimates \( T_c \) and underestimates \( J_c \). So at low temperatures, the inter-sublattice coupling \( K_c \) is roughly 300 times smaller than the intra-sublattice coupling \( J_c \).

Plotted in Fig. 3(b), the sublattice susceptibility \( \chi_{\text{sl}} \) rises sharply with increasing temperature and is roughly proportional to \( N_{\text{Cr}} \). The inter-sublattice coupling \( K_c(T) \) falls off almost linearly with temperature below 25 K. If \( K_c \) were short ranged and coupled sublattice moments at distinct points in space, we would expect that \( K_c(T) \propto M_{\text{sl}}(T)^2 \). The temperature dependence of \( K_c(T)/M_{\text{sl}}(T)^2 \) may be ascribed to the complex and long-ranged interaction between the two sublattices, each of which contains two species of magnetic ions with different temperature-dependent average moments.

Three of the four fitting parameters in this model, \( M_{\text{sl}}(T), N_{\text{Cr}}(T), \) and \( \chi_{\text{sl}}(T) \), are properties of the single-lattice compound; only \( K_c(T) \) reflects the presence of two sublattices. Above about 30 K, the fits break down primarily because the linear terms \( \chi_{\text{sl}}(T) \sin^2(\theta/2)H \) in the sublattice magnetization are no longer small compared to the zero-field value of \( 2\mu_B M_{\text{sl}}(T) \). Consequently, the inter-sublattice coupling \( K_c \) effectively depends on field as well as on temperature.

Despite the success of the fits below 30 K, the lower-

![FIG. 3: The fitting parameters versus temperature: (a) the number \( N_{\text{Cr}}(T) \) of Cr atoms in each magnetic cluser (the dashed curve gives the fit \( N_{\text{Cr}} = N_0[(T_c - T)/T_c]^{-3\nu} \) with \( \nu = 0.5 \) and the saturation magnetization \( 2\mu_B M_{\text{sat}}(T) \) and (b) the single-lattice susceptibility \( \chi_{\text{sl}}(T) \) and the inter-sublattice interaction \( K_c(T) \).]
The interpenetrating-lattice compound Cr(Ru$_2$)$_3$ may be the only known material with two or more weakly-interacting three-dimensional sublattices. Another molecule-based magnet that bears some similarities to Cr(Ru$_2$)$_3$ is methyleneamine chrome alums [13], which contains Cr(III) ions in a face-centered cubic structure. Although weak AF dipolar interactions couple the four sublattice moments, the intra-sublattice exchange is negligible in chrome alums. So the three-dimensional ordering takes place near $H_c(T)$ at nonzero temperatures, as observed in single crystals of conventional metamagnets [9, 10] up to about 85% of the Néel temperature.

Most of the puzzling properties of Cr(Ru$_2$)$_3$ with interpenetrating lattices can be explained by two macroscopic moments that are weakly AF coupled with a large energy barrier between the orientations of each moment. If the individual moments within each sublattice rotate together, the energy barrier between moments in the [111] and [111] directions for classical spins at $T = 0$ is $\Delta(0) = 0.07 J_s S^2 N_C$. At nonzero temperatures, we expect that $\Delta(T) \propto N_C J_s(T) M_{sl}(T)^2 J_c \sim N_C J_s(T_c - T)/T_c)^{-1/2}$. So $\Delta(T)$ will rise very close to $T_c$, which may explain the anomalous AC susceptibility observed in these materials.

Our work provides several new predictions for Cr(Ru$_2$)$_3$ with interpenetrating lattices. In the magnetic ground state, the total moment of each sublattice must lie along one of the four cubic diagonals. This can be verified by neutron scattering, either on a deuterated sample or with a large enough polycrystal. With a single crystal, the transitions between the AF and configurations I, II, or III should be observable for different orientations of the field. The predicted correlation length $\xi(T)$ can be verified independently by fitting the elastic peaks measured with neutron scattering, even on a polycrystalline sample. We hope that this paper will inspire future work on this fascinating system, including measurements on single crystals when they become available.

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