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Giant antiferromagnetically coupled moments in a molecule-based magnet with interpenetrating lattices

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The molecule-based magnet $[\mathrm{Ru_2(O_2CMe)_4}]_3[\mathrm{Cr(CN)_6}]$ contains two interpenetrating sublattices that behave like giant antiferromagnetically coupled moments with strong anisotropy. Because the sublattice moments only weakly depend on field, the volume of magnetically correlated clusters can be directly estimated from the field and temperature dependence of the magnetization while a polycrystalline sample undergoes a metamagnetic transition between antiferromagnetic and paramagnetic states.

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I. INTRODUCTION

Due to the importance of weak interactions that are commonly neglected in solid-state materials, molecule-based magnets display a variety of novel behavior.[1,2] One of the most fascinating molecule-based magnets exhibits an unusual "wasp-waisted" hysteresis loop that is attributed to the weak antiferromagnetic (AF) coupling between interpenetrating lattices of $[\mathrm{Ru_2(O_2CMe)_4}]_3[\mathrm{Cr(CN)_6}]$ (Me=methyl, $\mathrm{CH_3}$),[3–6] which we shall call $\mathrm{Cr(Ru_2)_3}$ for short. The shape of the initial $M(H)$ data[7] plotted in Fig. 1, with a shallow slope followed by a rapid rise, is usually associated with a metamagnetic transition between AF and paramagnetic (PM) states.[8] Metamagnetic transitions have been commonly observed both in solid-state systems like $\mathrm{FeCl_2}$ (Ref. 9) and DyAl garnet[10] as well as in other molecule-based magnets.[11] However, typical metamagnets do not also exhibit the nonzero remanent magnetization and coercive field found in the hysteresis loop of $\mathrm{Cr(Ru_2)_3}$ compounds with interpenetrating lattices below the transition temperature $T_c \approx 33$ K.

This paper demonstrates that a $\mathrm{Cr(Ru_2)_3}$ compound with interpenetrating lattices behaves like two giant AF coupled moments with a large energy barrier between the possible orientations of each moment. Quasi-one- or quasi-two-dimensional materials that magnetically order in three dimensions due to a weak coupling between sublattices are fairly common, even among molecule-based magnets.[12] We believe that $\mathrm{Cr(Ru_2)_3}$ is the only known material where each of the weakly interacting sublattices is fully ordered in three dimensions.

A single lattice of $\mathrm{Cr(Ru_2)_3}$ is sketched in Fig. 2(a), where every pair of Ru ions bridges two $[\mathrm{Cr(CN)_6}]^{3-}$ ions (labeled Cr for short) located at the corners of the cubic unit cell and separated by $a_l = 13.4$ Å. While each Cr(III) ion has a spin $S = 3/2$, each $\mathrm{Ru_2}$ dimer is in a II/III mixed-valence state with a total spin $S = 3/2$.[3] Due to the "paddle-wheel" molecular environment produced by the surrounding four Me groups sketched in Fig. 2(b), each $\mathrm{Ru_2}$ moment experiences a strong easy-plane anisotropy with $D \approx 100$ K or 8.6 meV.[13,14] The easy plane lies perpendicular to the axis joining the $\mathrm{Ru_2}$ sites with the neighboring Cr ions. Although a single-lattice $\mathrm{Cr(Ru_2)_3}$ compound has been synthesized,[5] the resulting samples are amorphous. A polycrystalline $\mathrm{Cr(Ru_2)_3}$ 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 properties of the interpenetrating-lattice compound can be explained by a simple model with strong easy-plane anisotropy D on the $\mathrm{Ru_2}$ sites, AF intrasublattice exchange J_c between neighboring Cr and $\mathrm{Ru_2}$ sites on each sublattice, and a weak AF intersublattice exchange K_c between moments on the two sublattices. The coupling K_c is the sum of the dipolar energy and the superexchange interaction through weakly overlapping molecular orbitals on the two sublattices.[15] Due to the weak coupling between sublattices, the volume $N_{\mathrm{Cr}} \sim \xi^3$ of magnetically correlated clusters directly affects the magnetization.

We have divided this paper into five sections. Section II provides the magnetic ground state and order parameters for the single-lattice compound. Section III focuses on the com-

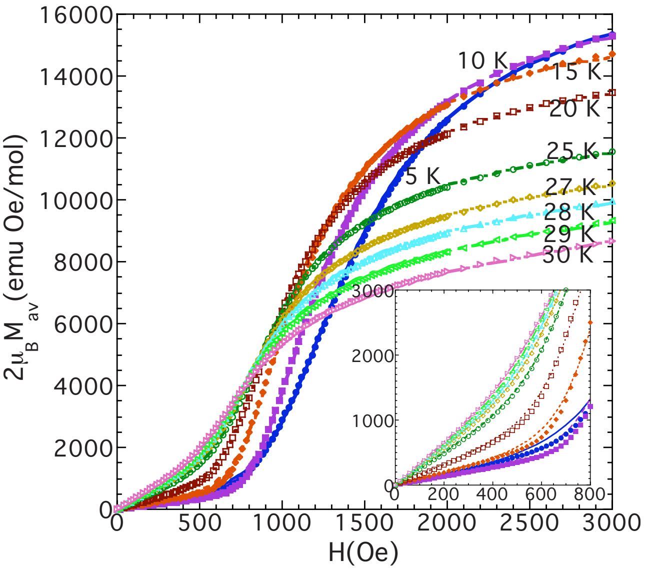

FIG. 1. (Color online) The initial magnetization (virgin curve) of $\mathrm{Cr(Ru_2)_3}$ with interpenetrating lattices for temperatures up to 30 K along with the predicted field dependence. As seen in the inset, small deviations occur near the critical fields with the theoretical curves lying slightly above the experimental data.

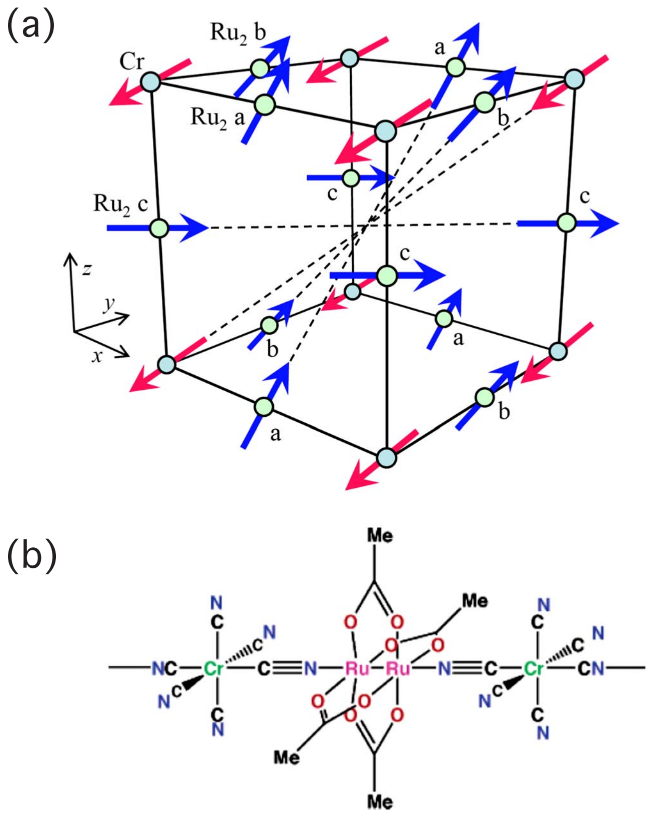

FIG. 2. (Color online) (a) The magnetic ground state of a single $\mathrm{Cr(Ru_2)_3}$ lattice for classical spins and large anisotropy with net moment in the [111] direction and (b) the molecular bond joining Cr and $\mathrm{Ru_2}$ ions with Me=methyl, $\mathrm{CH_3}$.

pound with interpenetrating lattices. Fits to the magnetization of the interpenetrating-lattice compound are discussed in Sec. IV. A brief conclusion is contained in Sec. V.

II. SINGLE-LATTICE COMPOUND

The key to understanding $\mathrm{Cr(Ru_2)_3}$ with interpenetrating lattices is to construct the correct ground state for the single-lattice compound. Each $\mathrm{Ru_2}$ spin pair in Fig. 2(a) 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 along the yz, xz, or xy planes, respectively. In the quantum case, the $\mathrm{Ru_2}$ 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 such as $\mathrm{Ho_2Ti_2O_7}$, where ferromagnetic order is frustrated by local [111] anisotropy.[16]

Both classical and quantum calculations provide the same magnetic ground state. The sum of the $\mathrm{Ru_2}$ 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 $M_{sl}=(\sqrt{6}-1)S\approx 1.45S$ per Cr ion.

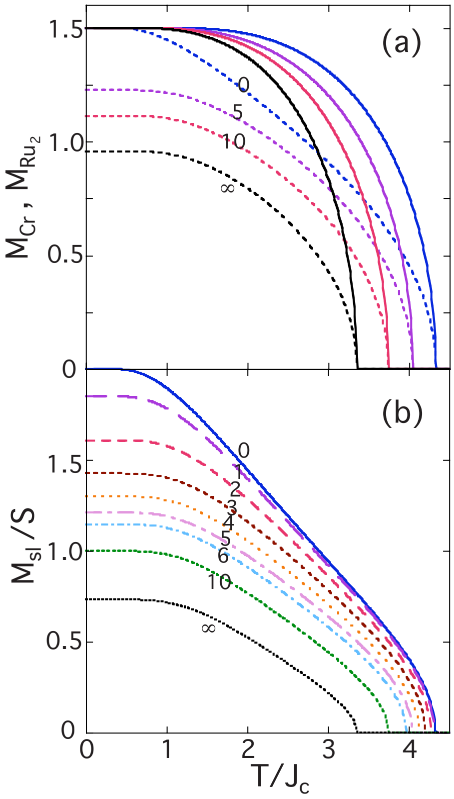

FIG. 3. (Color online) (a) The thermally averaged Cr (solid) and $\mathrm{Ru_2}$ (dashed) spins and (b) the sublattice magnetization $M_{sl}(T)$ versus T/J_c for quantum spins with the specified D/J_c.

Using mean-field (MF) theory with quantum spins, we obtain the expectation values of the Cr and $\mathrm{Ru_2}$ spins, $M_{\mathrm{Cr}}(T)$ and $M_{\mathrm{Ru_2}}(T)$, as well as the single-lattice moment $M_{sl}(T)$, which are plotted versus temperature in Figs. 3(a) and 3(b) for several values of D/J_c. Whereas $M_{\mathrm{Cr}}(0)=3/2$ for any D/J_c, $M_{\mathrm{Ru_2}}(0)$ decreases from 3/2 to 0.957 as D/J_c increases from 0 to ∞. If the thermally averaged $\mathrm{Ru_2}$ spin on the a sites (along the x axis) is $M_{\mathrm{Ru_2}}\mathbf{u}$ with $|u_y|=|u_z|$ and $|\mathbf{u}|=1$, then $u_x(T)$ weakly depends on temperature. We find that $|u_x(0)|=1/\sqrt{3}\approx 0.577$ when $D=0$, reaches a minimum of 0.159 at $D/J_c=9.6$, and approaches 0.174 as $D/J_c\rightarrow\infty$. Of course, $u_x(T)=0$ for classical spins with infinite anisotropy.

Generally, the sublattice moment is given by

$$M_{sl}=\sqrt{3}M_{\mathrm{Ru_2}}(\sqrt{2(1-u_x^2)}+|u_x|)-M_{\mathrm{Cr}}, \tag{1}$$

which reduces to $M_{sl}=\sqrt{6}M_{\mathrm{Ru_2}}-M_{\mathrm{Cr}}$ when $u_x=0$. For quantum spins, Fig. 3(b) indicates that with increasing D/J_c, $M_{sl}(0)$ decreases from $2S$ to $0.73S$ and T_c decreases from $4.35J_c$ to $3.36J_c$. For $D/J_c=5$, $T_c/J_c=4.05$, $M_{\mathrm{Ru_2}}(0)=1.23$, $|u_x(0)|=0.168$, and $M_{sl}(0)=1.21S$ per Cr ion.

Based on quantum MF calculations with $D/J_c=5$ and $J_c=1.72$ meV (see below), the single-lattice compound experiences a spin-flop transition at $H_{sf}\approx 2.78J_c/\mu_B\approx 80$ T with the field along one of the cubic diagonals. Above H_{sf}, the Cr and total $\mathrm{Ru_2}$ moments bend away from the cubic diagonal and, until all the moments become ferromagnetically (FM) aligned at an even higher field, the magnetization $2\mu_B\mathbf{M}$ is no longer parallel to $\mathbf{H}$.

III. INTERPENETRATING LATTICES

Now we are ready to consider $\mathrm{Cr(Ru_2)_3}$ with interpenetrating lattices. Because the intersublattice coupling K_c is much smaller than the intrasublattice coupling J_c and the metamagnetic critical field is much smaller than H_{sf}, the ground state of each sublattice can be considered to be rigid with very small deformations produced by the field. Hence, each sublattice has the same spin configuration as in Fig. 2(a) but with sublattice moments $M_{sl}\mathbf{n}_j$ ($j=1$ or 2) 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 ξ containing $N_{\mathrm{Cr}}\sim 2(\xi/a_l)^3$ Cr spins per cluster. Although ξ depends on field and may peak in the transition region, the polycrystalline nature of the $\mathrm{Cr(Ru_2)_3}$ samples suggests that the average value of ξ is most important. With N_{Cr} assumed independent of field, the energy is given by

$$E = N_{\mathrm{Cr}}\sum_i \{-\mu_B M_{sl}(\mathbf{n}_{1i}+\mathbf{n}_{2i})\cdot\mathbf{H} + 3K_cS^2\,\mathbf{n}_{1i}\cdot\mathbf{n}_{2i}\}, \qquad (2)$$

where $\mathbf{H}=H\mathbf{m}$ is the magnetic field and we sum over clusters i The intrasublattice exchange J_c only enters E through the sublattice moments $M_{sl}(T)$, which vanish above $T_c\propto J_cS^2$. The AF intersublattice interaction $K_c>0$ contains contributions from both the dipolar interactions between sublattices and the weak molecular overlap between transition-metal ions on different sublattices.[15]

The zero-field AF ground state is shown schematically in Fig. 4(b) with $\mathbf{n}_1=-\mathbf{n}_2$. Depending on the field orientation, the AF state becomes unstable to one of three possible spin configurations. Configuration III with $\mathbf{n}_1\cdot\mathbf{n}_2=-1/3$ appears at the critical field $H_c^{III}=\sqrt{3}K_cS^2/(\mu_B M_{sl})$ when $\mathbf{m}=[111]$. For $\mathbf{m}=[110]$, configuration II with $\mathbf{n}_1\cdot\mathbf{n}_2=1/3$ appears at the field $H_c^{II}=\sqrt{6}K_cS^2/(\mu_B M_{sl})$. For $\mathbf{m}=[111]$, configuration I (the PM state) with $\mathbf{n}_1=\mathbf{n}_2=\mathbf{m}$ appears at the field $H_c^{I}=3K_cS^2/(\mu_B M_{sl})$.

To compare our results with measurements on polycrystalline samples, the moment is averaged over all field directions. It is straightforward to show that at $T=0$,

$$\frac{M_{av}}{M_{sat}} = 1-\left(\frac{H_c}{H}\right)^2, \qquad H>H_c, \qquad (3)$$

where M_{av} and M_{sat} are the average and saturation moments per Cr ion, respectively, and $H_c=H_c^{III}$ is the smallest of the three critical fields. Plotted in Fig. 4(a), this form for the magnetization is also found in a single-domain magnet with finite anisotropy.[17] For classical spins with infinite anisotropy, $\mu_B H_c\approx 1.20K_cS$ and $M_{sat}=\sqrt{3}M_{sl}/2\approx 1.25S$. The stable phases are shown in Fig. 4 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 (configuration I).

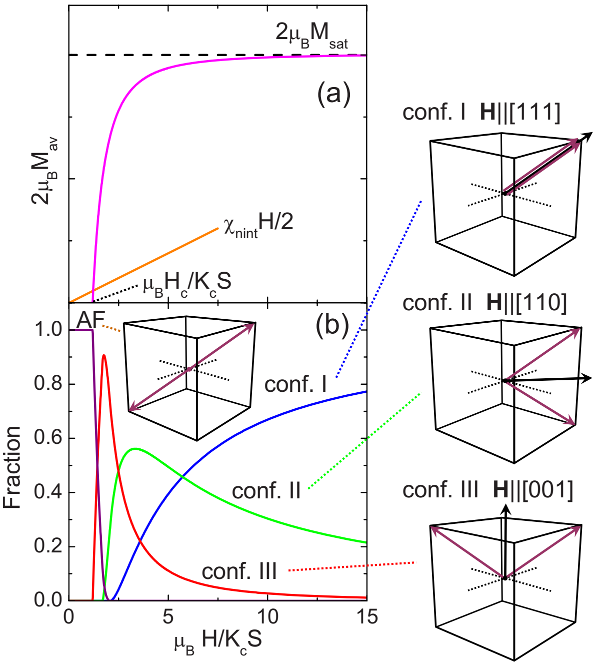

FIG. 4. (Color online) (a) The $T=0$ average moment and noninteracting linear susceptibility $\chi_{nint}H/2$ and (b) the fractions of the AF state and configurations I, II, and III versus $\mu_B H/K_cS$ assuming classical spins and large anisotropy.

We must modify Eq. (2) to account for the small distortion of the single-lattice ground state with field. This 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 $\mathrm{Ru_2}$ spins can easily cant toward 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 noninteracting susceptibility of the magnetic configuration $\{\mathbf{n}_1,\mathbf{n}_2\}$ is then given by $\chi_{nint}=\chi_1+\chi_2$ per pair of Cr atoms and the additional linear term in the magnetization is $N_{\mathrm{Cr}}\chi_{nint}H/2$. The extra term $-N_{\mathrm{Cr}}\chi_{nint}H^2/4$ must then be added to the energy E of Eq. (2) for each cluster.

In the AF state with $\mathbf{n}_1=-\mathbf{n}_2$, $\theta_2=\theta_1+\pi$ and $\chi_{nint}=\chi_{sl}$. In the PM state with $\theta_1=\theta_2$, $\chi_{nint}=2\chi_{sl}\sin^2(\theta_1/2)$ vanishes when $\theta_1=0$ but is nonzero when $\mathbf{H}$ points away from a cubic diagonal. Averaged over all field directions, the susceptibility in the PM phase is $\chi_{nint}\approx 0.134\chi_{sl}$. In agreement with experiments,[4,7] the differential susceptibility at high fields is much smaller than the the linear susceptibility at low fields.

IV. FITTING PARAMETERS AND MAGNETIC CORRELATIONS

Using this model, we evaluate the partition function by summing over the 64 configurations of $\{\mathbf{n}_1,\mathbf{n}_2\}$ and the magnetization by averaging over field directions. For every tem-

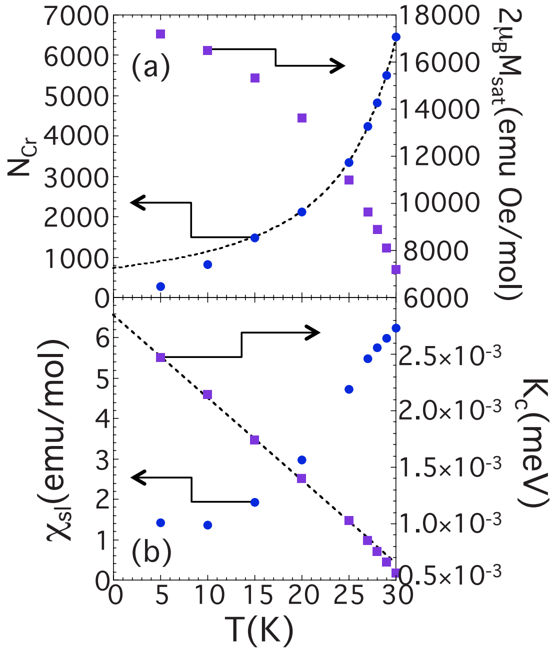

FIG. 5. (Color online) The fitting parameters versus temperature: (a) the number $N_{\mathrm{Cr}}(T)$ of Cr atoms in each magnetic cluster [the dashed curve gives the fit $N_{\mathrm{Cr}}=N_0[(T_{\mathrm{c}}-T)/T_{\mathrm{c}}]^{-3\nu}$ with $\nu=0.5$] and the saturation magnetization $2\mu_B M_{sat}(T)$ and (b) the single-lattice susceptibility $\chi_{sl}(T)$ and the intersublattice interaction $K_c(T)$.

perature, the average magnetization depends on four parameters: the single-lattice susceptibility χ_{sl}, the sublattice moment M_{sl}, the weak AF interaction K_c between sublattices, and the number N_{Cr} of Cr atoms within each cluster, half belonging to each sublattice. The fits are provided in Fig. 1 and the resulting parameters are plotted in Fig. 5.

In Fig. 5(a), $N_{\mathrm{Cr}}(T)$ is consistent with the functional form $N_{\mathrm{Cr}}(T)=N_0[(T_{\mathrm{c}}-T)/T_{\mathrm{c}}]^{-3\nu}$, where $N_0\approx725$, $T_{\mathrm{c}}=39$ K, and $\nu=0.5$, which is the MF value for the critical exponent. Since the functional form $\xi(T)\propto[(T_{\mathrm{c}}-T)/T_{\mathrm{c}}]^{-\nu}$ is only expected close to T_{c}, it is remarkable that deviations from this form only appear below about 15 K. Other evidence for the MF nature of the phase transition in $\mathrm{Cr(Ru_2)_3}$ comes from the magnetization of the single-lattice compound,[4] which, although amorphous, closely follows a Brillouin function and vanishes near T_{c} like $(T_{\mathrm{c}}-T)^{1/2}$. It is likely that the fitting parameter T_{c} in the correlation volume $N_{\mathrm{Cr}}(T)$ exceeds the true transition temperature $T_{\mathrm{c}}\approx33$ K because the correlation length ξ is cut off by the finite particle size or by other imperfections in the sample.

The "saturation" magnetization $2\mu_B M_{sat}(T)=\sqrt{3}\mu_B M_{sl}(T)$ per Cr atom plotted in Fig. 5(a) gives the average magnetization when the two nondistorted 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 17 200 emu Oe/mol. In rough agreement with the assumed form for the noninteracting susceptibility χ_{nint}, 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 $N_{\mathrm{Cr}}=6464$ have a correlation length $\xi\sim15a_l=200$ Å and a sublattice magnetization $\mu_B N_{\mathrm{Cr}} M_{sl}(T=30\ \mathrm{K})\approx4500\mu_B$.

At $T=5$ K, the saturation magnetization is significantly lower than the classical result with $D=\infty$. But as shown in Fig. 3(b), the single-lattice moment $M_{sl}(0)$ 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 $D/J_c\approx5$ and $J_c\approx1.72$ meV. Another estimate for J_c comes from the MF result $T_{\mathrm{c}}\approx4.05J_c=33$ K for the transition temperature with $D/J_c=5$ yielding the smaller value $J_c\approx0.70$ meV. However, MF theory typically overestimates T_{c} and underestimates J_c. We conclude that the intersublattice coupling K_c is roughly 600 times smaller than the intrasublattice coupling J_c at low temperatures.

Plotted in Fig. 5(b), the sublattice susceptibility χ_{sl} rises sharply with increasing temperature and is roughly proportional to N_{Cr}. The intersublattice 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 $K_c(T)\propto M_{sl}(T)^2$. The temperature dependence of $K_c(T)/M_{sl}(T)^2$ 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, $M_{sl}(T)$, $N_{\mathrm{Cr}}(T)$, and $\chi_{sl}(T)$, are properties of the single-lattice compound; only $K_c(T)$ reflects the presence of two sublattices. The fits break down above 30 K primarily because the linear terms $\chi_{sl}(T)\sin^2(\theta/2)H$ in the sublattice magnetization are no longer small compared to the zero-field value of $2\mu_B M_{sl}(T)$. Consequently, the intersublattice coupling K_c effectively depends on field as well as on temperature.

Despite the success of the fits below 30 K, the inset to Fig. 1 suggests one limitation of this model. Although the correlation length ξ must reach a maximum near $H_c(T)=\sqrt{3}K_c(T)S^2/(\mu_B M_{sl}(T))$ as fluctuations soften, our model assumes that $\xi(T)$ is independent of field. Consequently, the curves in Fig. 1 lie slightly above the data points near $H_c(T)$, especially at lower temperatures. A correlation length $\xi(T,H)$ that peaks in the vicinity of $H_c(T)$ would produce even better agreement with the experimental data. Since the thermal averages are assumed to be independent from one cluster to another, the model magnetization is a continuous function of H for any nonzero temperature and for any orientation of the magnetic field. Due to the polycrystalline sample, we cannot say whether the experimental magnetization of $\mathrm{Cr(Ru_2)_3}$ experiences a jump 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.

V. CONCLUSION

The interpenetrating-lattice compound $\mathrm{Cr(Ru_2)_3}$ may be the only known material with two or more weakly interacting three-dimensional sublattices. Another molecule-based magnet that bears some similarities to $\mathrm{Cr(Ru_2)_3}$ is methylamine chrome alums[18] which contains Cr(III) ions in a face-centered cubic structure. Although weak AF dipolar interactions couple the four sublattice moments, the intrasublattice exchange is negligible in chrome alums. Hence, the three-dimensional ordering at about 0.02 K is also produced by the dipolar interactions between magnetic sublattices.

Most of the puzzling properties of $\mathrm{Cr(Ru_2)_3}$ 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, then the energy barrier between moments in the $[111]$ and $[11\bar{1}]$ directions for classical spins at $T=0$ is $\Delta(0)=0.035J_cS^2N_{\mathrm{Cr}}$. At nonzero temperatures, we expect that $\Delta(T) \propto N_{\mathrm{Cr}}(T)M_{sl}(T)^2J_c \sim N_0J_c[(T_c-T)/T_c]^{-1/2}$. So $\Delta(T)$ will rise very close to T_c which may explain the anomalous ac susceptibility[3] observed in these materials.

Our work provides several predictions for $\mathrm{Cr(Ru_2)_3}$ 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 with a deuterated sample or a large 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 for 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.

ACKNOWLEDGMENTS

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[15] For easy-plane anisotropy, the Cr-Cr dipolar interactions between sublattices cancel by symmetry while the Cr-$\mathrm{Ru_2}$ and $\mathrm{Ru_2}$-$\mathrm{Ru_2}$ dipolar interactions produce intersublattice interactions that are AF and FM, respectively, with a net FM dipolar interaction between sublattices. At low temperatures, the observed AF interaction K_c can be recovered with an additional intersublattice superexchange between neighboring $\mathrm{Ru_2}$ pairs separated by $a_l/2$ of 3.1×10^{-3} meV, using the sublattice ground state provided by a quantum calculation with $D/J_c=5$.

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