Magnetism of Cr_{10} wheels on Au(111) and Cu(111) surfaces

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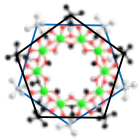
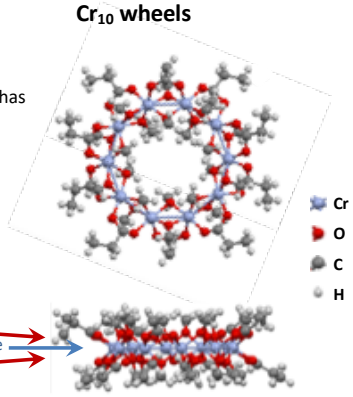
Molecular Precursors: Cr_{10} wheels

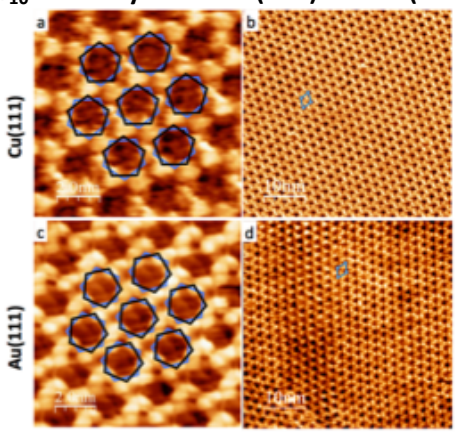
$\{Cr_{10}(OMe)_{20}(O_2CCMe_3)_{10}\}$ wheel, side and front views.

Local D_{5d} symmetry of carboxylate ligands (below) has been outlined by lines.





Cr_{10} monolayers on Au(111) and Cu(111)



STM images of Cr_{10} on Cu(111) and Au(111)

Local D_{5d} symmetry close-packed model is superimposed on high resolution STM image and quasi-hexagonal unit cell is evidenced on large scale images.

a) 10×10 nm², 1200 mV, 0.092nA,
b) 50×50 nm², 875 mV, 1.500 nA,
c) 10×10 nm², 1300 mV, 0.200 nA,
d) 50×50 nm², 1300 mV, 0.200 nA

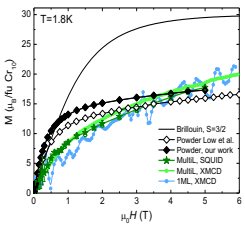
The wheels self assemble in an ordered hexagonal structure, as outlined by the unit cell in Figs. b and c.

The wheels retain their structure and exhibit the expected 5-fold symmetry: At each $\{Cr_{10}\}$ molecule position, the black pentagons evidence the bright spots (with average edge of 10 Å) attributed to the tert-butyl groups of the carboxylate ligands above the equatorial metal plane and a second blue pentagon rotated by 36° with respect to the former, can be ascribed to the tert-butyl groups below the metal plane.

The close-packed, quasi-hexagonal 2D network, and the high resolution STM contrast are very similar the earlier described for $\{Cr_{10}\}$/Ag(110) Escriba aquí la ecuación.

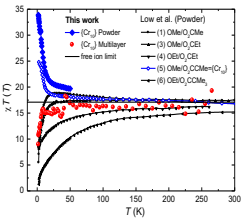
Magnetic Properties

Magnetization

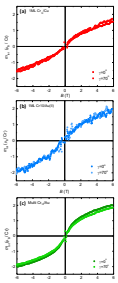


Field dependence of the magnetization. Comparison of Cr_{10}/Au grafted samples (1monoL, 14-MultiL and 300-MultiL) vs. bulk powdered samples (this work and Low et al.)

Susceptibility

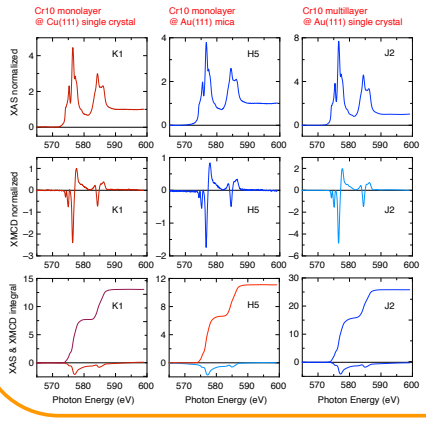


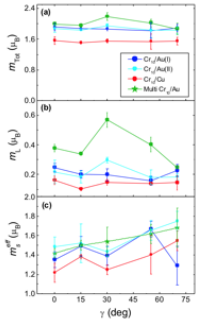
Susceptibility product χT for 300-MultiL Cr_{10}/Au and Powder sample in this work, compared with reported data by **Low et al**. for Cr_{10} rings with different ligands (ring 5 coincides with $\{Cr_{10}\}$ in this work)



Field dependence of the XMCD per Cr atom at γ=0°, 70° T=2K
(a) 1ML Cr_{10}/Cu,
(b) 1ML Cr_{10}/Au(II), and
(c) MultiLayer Cr_{10}/Au.

XMCD Measurements

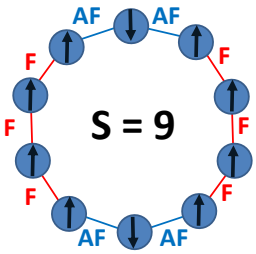




Effective spin, orbital moment ant total magnetic moment per Cr atom as a function of the beam incidence angle at B=6T, T=1.8K, for the four characterized samples: 1ML Cr_{10}/Au(I), 1ML Cr_{10}/Au(II), 1ML Cr_{10}/Cu and MultiL Cr_{10}/Au.

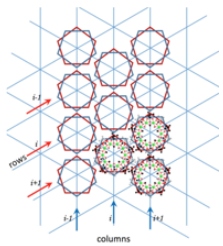
MonteCarlo and analitycal calculations

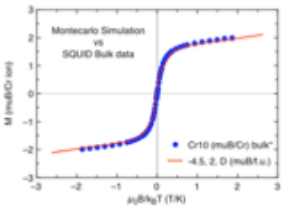
Evaporation of {Cr10} onto a substrate producing subtle structural changes induce strong changes in the Cr-Cr interactions and **definitely different magnetic behavior than the bulk.**

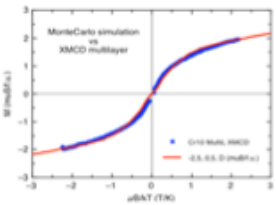


Montecarlo simulations show that the magnetic evolution can be explained by {Cr10} molecules magneticaly consisting of two ferromagnetic semi-crowns containing 4 Cr ions, separated by 2 Cr ions with antiferromagnetic interactions, giving rise to the ground S = 9 state, in agreement with EPR data in literature [Sharmin 2015]. (*incorrectly*-) Asymmetric rings were introduced by Low et al. to explain the INS spectra. Our work takes into account inversion symmetry of the molecule, giving rise to a limited set of possible spin ground states (S=15, 9, 3, 3', 0, 0')

Analytic calculations performed with the code MAGPACK code for a 6-Cr ring achieved results similar to MonteCarlo, but the size of the ring was limited to 6 by memory limitations.







CONCLUSIONS

- The magnetic behavior of the bulk and the deposited molecules notably changes, from overall FerroMagnetic to AntiferroMagnetic
- STM microscopy combined with XMCD and SQUID magnetometry and ad-hoc MonteCarlo simulations allow to understand the microscopic origin of the differences between {Cr10} samples.
- Ferromagnetism in {Cr10} is not only quite weak, but rather unstable, as the deposited samples are globally antiferromagnetic

References

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