

H7. SPIN REDISTRIBUTION BY ENTANGLEMENT IN AN ORGANIC MAGNET

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A fundamental feature of quantum mechanics is entanglement, defined as a physical realization of linear superpositions of simple multi-particle states [1]. Entangled particles are physically interdependent even though they may be spatially separated. Entanglement of spin degrees of freedom in molecular magnets holds great promise for spintronics devices [2]. Rather complex entangled states are realized in applied magnetic fields. For each magnetic group of atoms the spin is quantized, and the magnetization can have only discrete values. Due to entanglement though, the spin density can be arbitrarily re-distributed, resulting in seemingly paradoxical fractional local magnetization. Recent experiments on the 5C1 and 6T2 [6] polarized neutron diffractometers at the ORPHEE reactor yielded a direct quantifiable experimental observation of this effect in a novel organic molecular magnet.

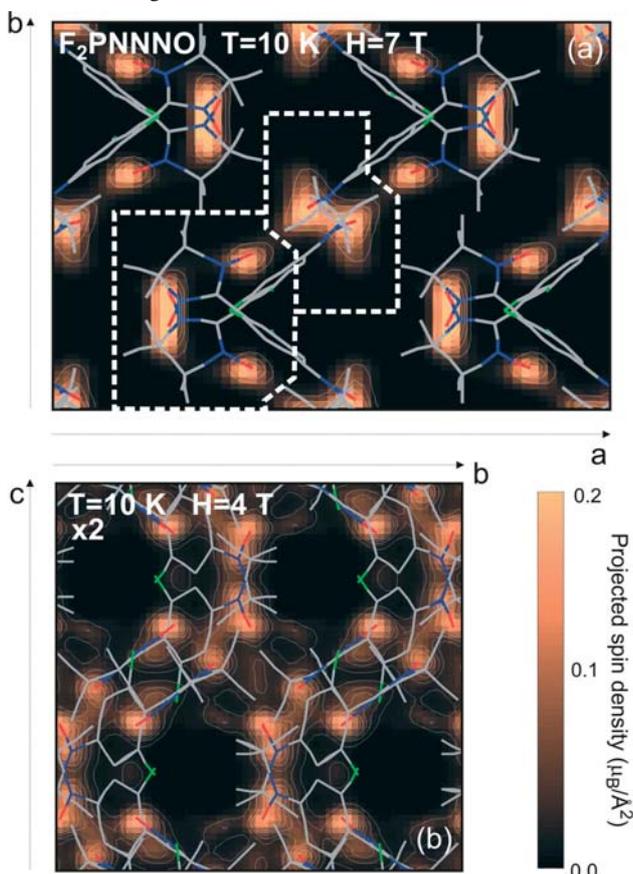


Figure 1. Experimental spin density distribution in a F_2PNNNO spin-tetramer at $T = 10$ K, as reconstructed using the Maximum Entropy method. Areas outlined with thick dashed lines were used to estimate the spin populations on the nitronyl nitroxide and *tert*-butyl nitroxide.

Our model material, 2-[2,6-difluoro-4-(*N-tert*-butyl-*N*-oxyamino)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide, F_2PNNNO for short, is a prototypical spin tetramer system [3]. The magnetic properties are due to two unpaired electrons that reside in p^* antibonding molecular orbitals of the nitronyl nitroxide (NN) and the *tert*-butyl nitroxide (tBuNO) groups, respectively. These $S = 1/2$ spins are coupled via a ferromagnetic intramolecular exchange constant $J_F \sim 35$ meV.

When in crystalline form, F_2PNNNO molecules are arranged in pairs, so that their tBuNO groups are close enough for AF interactions of magnitude $J^{AF} \sim 5.8$ meV. The result is a two-molecule unit containing four interacting spins. Its unique ground state is a non-magnetic singlet. In the presence of an external magnetic field applied along the z axis, the excited state with the lowest energy has a total spin $S_{total} = 1$ and a spin projection $S_z = +1$. We shall denote this state as $|1, +1\rangle$. Its wave function is heavily entangled: by diagonalizing the Heisenberg Hamiltonian of the tetramer we find that it actually is a linear combination of four "pure" (non-entangled) spin wave functions: $|1, +1\rangle = a|\underline{\quad}\rangle + b|\underline{\quad}\rangle - a|\underline{\quad}\rangle - b|\underline{\quad}\rangle$, where $a \sim 0.46$ and $b \sim 0.54$. The most striking consequence of this entanglement is an imbalanced spin density distribution $S_z(\mathbf{r})$: the local spin populations of the NN groups are equal, but different from those of the tBuNO groups. The ratio R of these spin populations is given by $R = a^2/b^2 \sim 1.39$. If entanglement was absent, and only pure spin-projection states were allowed, then, due to the weakness of the central antiferromagnetic bond, the lowest-energy excited state would have been $|\underline{\quad}\rangle$, with $R_{pure} = 1$. If quantum mechanics failed altogether, the spins would behave as classical moments. They would align themselves in the (x, y) plane and tilt slightly in the field direction. It is easy to show that the resulting imbalance in $S_z(\mathbf{r})$ would be minuscule: $R_{classical} = 1 + |J_{AF}|/4|J_F| = 1.04$. Thus, a large imbalance of NN and tBuNO spin densities in F_2PNNNO can be considered a *signature of spin entanglement*.

To prepare the tetramer in its $|1, +1\rangle$ excited state high magnetic fields of $H = 7$ T or $H = 4$ T were used to lower its energy as much as possible. The data were then taken at an elevated temperature of $T = 10$ K that made this state partially populated. The main technical challenge of measuring the spin density distribution is the very small total magnetization, estimated at less than half a Bohr magneton for the 2-molecule unit comprising about 100 atoms. Polarized neutron in the crystal.

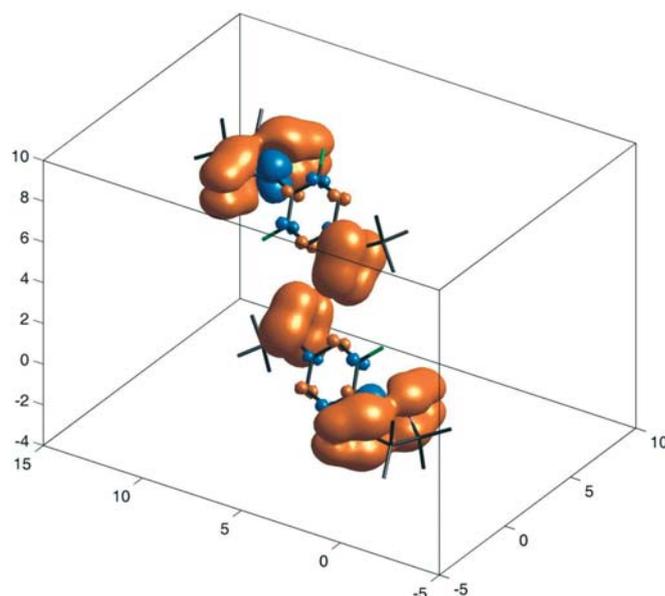


Figure 2 Experimental spin density distribution in a F₂PNNNO spin-tetramer at T = 10 K at H = 7 T and T = 10 K, as reconstructed using atomic orbital expansion. The isosurfaces are drawn at $1 \times 10^{-3} \mu_B/\text{\AA}^3$ (orange) and $-1 \times 10^{-3} \mu_B/\text{\AA}^3$ (blue) levels. The axes show Cartesian coordinates in Angstroms.

In the experiments the so-called flipping ratios of 70 Bragg reflections were measured. Maximum entropy (Fig. 1) and atomic orbital expansion (AOE, Fig. 2) were used to reconstruct the real-space magnetization distribution.

A very good measure of the reliability of the AOE reconstruction is its result for the total tetramer magnetization: $m = 0.48(2) \mu_B$ and $m = 0.28(2) \mu_B$, for $H = 7$ T and $H = 4$ T, respectively. These values are consistent with existing bulk susceptibility data, and are in excellent agreement with a thermodynamic quantum-mechanical calculation for a single tetramer: $m = 0.59 \mu_B$ and $m = 0.32 \mu_B$, respectively. With this assurance of the validity of our approach, we obtain experimental estimates for the imbalance between the NN and tBuNO spin populations: $R = 1.53(3)$ and $R = 1.51(2)$, for $H = 7$ T and $H = 4$ T. The quantitative agreement with theoretical predictions for entanglement-induced spin redistribution in F₂PNNNO is remarkable.

Our polarized neutron diffraction results not only provide a direct evidence of spin entanglement, but also help understand the microscopic interactions that cause it. In Fig. 2, note the negative density in the vicinity of the apical carbon atom of the NN group. This large negative spin population [4] plays a key role in the ferromagnetic intra-molecular coupling J_F . It is a part of a sign-alternating spin density wave that propagates across the phenyl ring and connects the positively populated N sites of the NN and tBuNO fragments over a large distance. This density-wave mechanism is analogous to Ruderman-Kittel-Kasuya-Yosida interactions in metals.

AF interactions J_{AF} between tBuNO groups of the two molecules comprising each tetramer span a shorter distance, and are more conventional in nature. They are due to direct exchange and arise from molecular orbital overlap.

The simplicity and isotropic nature of delocalized magnetic *sp*-electrons in organic molecules make them useful as a testing ground for fundamental quantum mechanics. In the particular case of F₂PNNNO we are able to detect and precisely quantify the redistribution of spin density caused by entanglement of four interacting quantum spins, and learn about the microscopic mechanisms of these entangling interactions.

A full report on this study can be found in Ref. [5].

- [1] Mermin, N. D., *Physics Today* **38**, 38 (1985).
- [2] Leuenberger, M. N. and Loss, D., *Nature* **410**, 789 (2001).
- [3] Hosokoshi, Y., Nakazawa, Y. and Inoue, K., *Phys. Rev. B* **60**, 12924 (1999).
- [4] Davis, M. S., Morokuma, K. and Kreilick, R. W., *J. Am. Chem. Soc.* **94**, 5588 (1972).
- [5] A. Zheludev, V. O. Garlea, S. Nishihara, Y. Hosokoshi, A. Cousson, A. Gukasov and K. Inoue, cond-mat/0609299.
- [6] A. Gukasov, A. Goujon, J.-L. Meuriot, C. Person, G. Exil and G. Koskas, *Physica B, Proceedings of PNCMI-2006*, Berlin (see also in this report).