MAGNETIC NANOSTRUCTURES

Quantum chains with a spin

The ability to access experimentally the quantum-mechanical nature of the interaction between single atomic spins opens windows onto the most fundamental magnetic phenomena.

PIETRO GAMBARDELLA

is at the Catalan Institute for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, E-08010 Barcelona, and Catalan Institute of Nanotechnology (ICN), UAB Campus, E-08193 Bellaterra, Spain.

e-mail: pietro.gambardella@icrea.es

Today's rate of computing speed and storage capacity is the outcome of 50 years of continuous research in materials science, aimed at controlling the flow of charge and spin information to and from smaller and smaller structures. Although the electron spin is essentially a quantum-mechanical phenomenon, the magnetization vector resulting from the alignment of neighbouring spins in the atoms that constitute a magnetic bit has always been treated as a classical quantity, that is, possessing a well-defined orientation and value. But what happens as conventional micromagnetic models and nanostructured materials are reduced to atomic dimensions? This picture might fail entirely and yet open exciting new pathways for understanding and manipulating magnetism in solid-state systems. Cyrus Hirjibehedin and colleagues at IBM have recently reported in *Science* the fabrication of Mn nanoparticles in the form of linear chains that display truly collective quantum behaviour[1]. Using a local spin-excitation spectroscopy technique, the IBM team was able to show how the quantum properties of this system depend on the number of atoms involved and on the fine-tuning of material parameters, such as the mixing of electronic states between chain and substrate, and the interaction between Mn spins. They demonstrated an innovative method to measure and control these magnetic interactions.

Manganese atoms in bulk crystals tend to align antiferromagnetically, retaining this tendency also in clusters comprising only a few atoms[2]. In a one-dimensional antiferromagnetic chain, adjacent spins couple in opposite directions. This gives rise to zero (compensated) or non-zero (uncompensated) magnetization states for chains containing an even or odd number of atoms (Fig. 1a). Or at least we tend to think this way. Even though the configurations described above correctly represent the ground state of an antiferromagnetic chain in the classical limit — the so-called Néel state — quantum-mechanical predictions are remarkably different. According to the

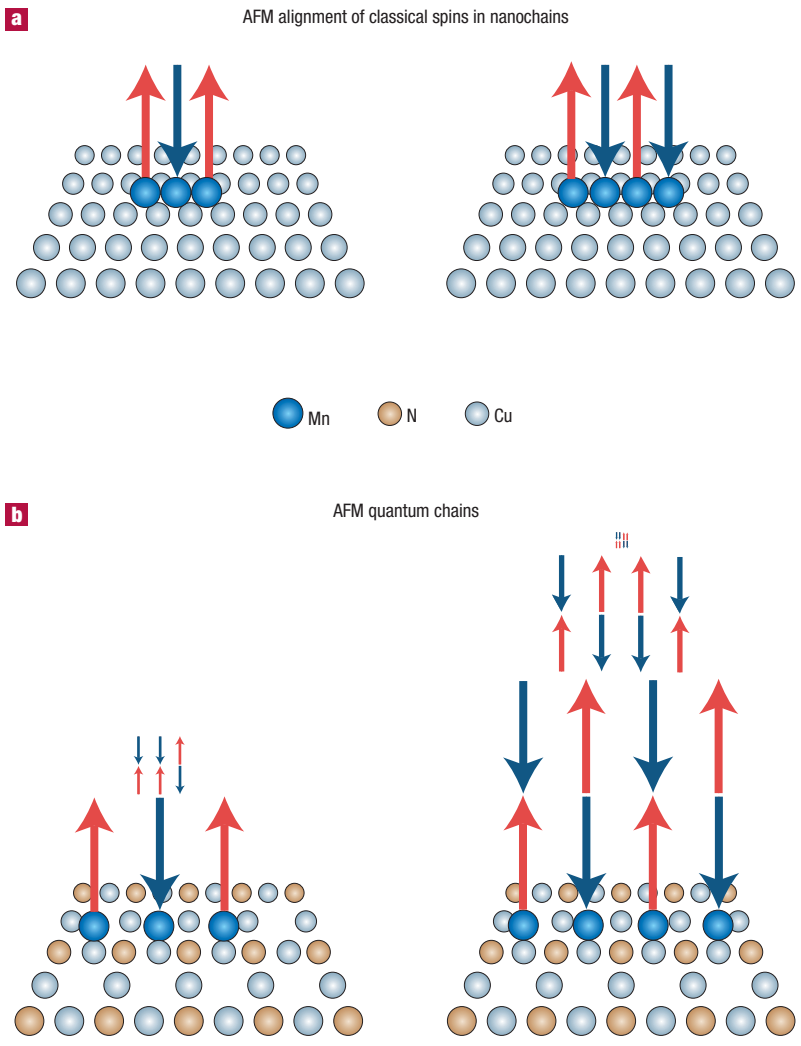

Figure 1 Spin states in classical and quantum atomic chains with $N = 3, 4$ atoms, corresponding to uncompensated and compensated magnetic moments, respectively. **a**, Classical antiferromagnetic order. Arrows represent the orientation of individual atomic spins. **b**, Quantum chains: individual spins are entangled, their value is given by a superposition of states. The ground state for $N = 3, 4$ chains of spin 1/2 is shown as a sum of spin configurations, where the arrow length represent the probability weight of each configuration. With larger spin (3/2, 5/2, ...) the number of configurations increases.

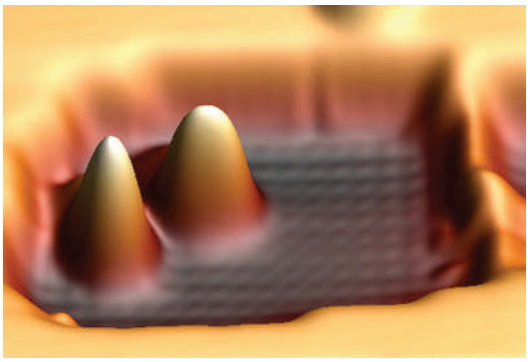

Figure 2 STM image of a single Mn atom (foreground) and an $N = 2$ chain of Mn atoms (background) on the CuN substrate. The STM measures the electron density surrounding each atom, showing Mn as bumps and the insulating CuN layer as a depression with respect to the surrounding plain Cu surface. The field of view is 78×78 Å^2.

Heisenberg model, which is used for antiferromagnetic chains with nearest-neighbour exchange interaction J, the chain is described by a superposition of states, each representing a classical spin configuration (Fig. 1b). As a consequence, individual atomic spins are 'entangled', that is, it is not possible to define the orientation of any of them irrespectively of the others. Such an effect is well known in the case of other quantum-mechanical systems, for example, a covalent molecular bond, but obtaining direct evidence in low-dimensional magnetic systems such as quasi-one-dimensional and two-dimensional crystals has been hampered by sample and measurement restrictions[3]. Yet, if entangled spins could be arranged at leisure on a substrate, we would be able to study and eventually harness their quantum behaviour much more easily. Hirjibehedin and colleagues used an elegant bottom-up approach to make progress in this direction.

First, they showed that a Mn antiferromagnetic chain can be constructed atom by atom on a supporting surface, retaining almost ideal collective quantum properties. To create atomically thin chains of up to 10 atoms in length, the researchers used the tip of a low-temperature scanning tunnelling microscope (STM) to move Mn atoms into position on an electrically insulating monolayer film (Fig. 2). The choice of Mn and substrate was no trivial task, as the mixing (or hybridization) of electronic orbitals between transition-metal and substrate atoms normally reduces the moment of a magnetic impurity and induces its spin S to behave classically[4]. Owing to the absence of conduction electrons, an insulating substrate minimizes this effect, but the surface corrugation poses a problem for moving and positioning atoms by STM. The IBM team tested Al_2O_3 and NaCl thin films before successfully using a CuN monolayer (A. J. Heinrich, private communication). Mn was selected by virtue of its half-filled outer orbital shell ($3d$), which corresponds to a stable and isotropic magnetic moment, entirely given by the electronic spin ($S = 5/2$). To probe the spin state of the chains, the authors combined the imaging and manipulation capabilities of STM with a technique they recently developed to measure local spin-excitations using inelastic tunnelling spectroscopy[5]. This technique is similar in principle to electron spin resonance spectroscopy (ESR), but allows for single-atom sensitivity and spatial resolution. Electrons tunnelling from the STM tip to the sample, like ESR photons, can transfer energy and angular momentum to the spin system, inducing well-defined transitions between quantum states of the Mn chains. Such spin-flip excitations allowed the authors to map the chain's total spin, exchange coupling, and magnetic anisotropy as a function of the size and position on the surface. Most interestingly, the STM spectra did not change when recorded on different positions along the chains, confirming that the spin states are a collective property of the whole system and not of individual atoms.

If this is so, why can classical antiferromagnetic alignment be imaged at all — also by STM and with atomic resolution — as shown recently by Heinze *et al.*[6] for a Mn monolayer on tungsten? The answer might reside in the extended lateral dimensions of the Mn film that could stabilize magnetic order[7], but also in the stronger electronic hybridization between Mn and tungsten compared with CuN, or in the possible presence of ferromagnetic defects that pin the Mn moments down to a specific orientation. The variety of the above scenarios expounds the fascinating diversity in the synthesis and exploitation of magnetic nanostructures. Whereas classically ordered antiferromagnetic layers are an essential component of exchange-biased materials[8] used in the fabrication of sensitive magnetic field sensors, antiferromagnetic quantum chains have been proposed as archetypal spin-cluster qubits for quantum-computation purposes[9,10]. Much remains to be done in this field, notably to understand how changes in the substrate environment affect the quantum spin states of the system, and how to couple chain ensembles. Not only have Hirjibehedin *et al.* shown that it is possible to assemble quantum spin structures on a surface, but they also provided a method of reading and modifying their spin states to investigate the most fundamental magnetic interactions in matter. No doubt this will turn out to be valuable both in the classical and quantum world.

REFERENCES

1. Hirjibehedin, C. F., Lutz, C. P. & Heinrich, A. J. *Science* published online 30 March 2006 (doi:10.1126/science.1125398).
2. Van Zee, R. J., Baumann, C. A. & Weltner, W. Jr *J. Chem. Phys.* **74,** 6977–6978 (1981).
3. De Jongh, L. J. & Miedema, A. R. *Advan. Phys.* **23,** 1–260 (1974).
4. Gambardella, P. *et al. Science* **300,** 1130–1133 (2003).
5. Heinrich, A. J, Gupta, J. A., Lutz, C. P., & Eigler, D. M. *Science* **306,** 466–469 (2004).
6. Heinze, S. *et al. Science* **288,** 1805–1808 (2000).
7. Fröhlich, J. & Lieb, E. H. *Phys. Rev. Lett.* **38,** 440 (1977).
8. Kuch, W. *et al. Nature Mater.* **5,** 128–133 (2006).
9. Meier, F., Levy, J. & Loss, D. *Phys. Rev. Lett.* **90,** 047901 (2003).
10. Meier, F., Levy, J. & Loss, D. *Phys. Rev. B* **68,** 134417 (2003).