

## MAGNETIC NANOSTRUCTURES

## Overcoming thermal fluctuations

The storage density of computer hard drives has increased to the point that magnetic recording media is cheaper than paper. Yet there are limits to this technology. As they decrease in size, magnetic 'bits' become thermally unstable, providing a challenge to further miniaturization.

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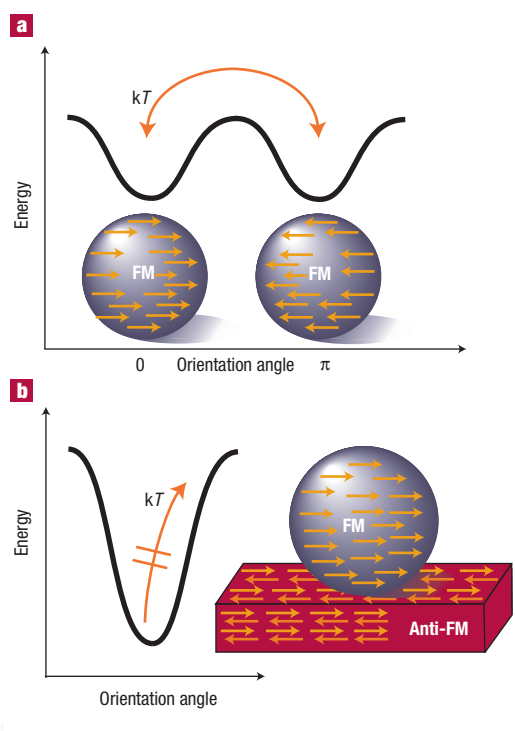
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Systems that undergo phase transitions experience random thermal fluctuations. These fluctuations are generally largest close to the phase-transition temperature, and smaller at lower temperatures. But when the system itself is small, the energy required for the phase transition becomes comparable to the thermal energy, thus lowering substantially the temperature of the transition. In particular, the magnetic energy stored in a small, nanoscale (typically a few tens or hundreds of nanometres) magnetic particle is comparable to the thermal energy. Hence, a nanomagnet may become non-magnetic (superparamagnetic) at a so-called blocking temperature, at which it would be magnetic in the bulk<sup>1</sup>. A fundamental question in nanomagnetism is "Can this superparamagnetism be avoided?". The answer also has important implications for the sensor and storage industries<sup>2</sup>. Writing in *Nature*, Vassil Skumryev and colleagues<sup>3</sup> demonstrate a possible solution to this problem for small Co particles.

Nanostructured magnets have interesting physical properties and are being studied intensely, owing to their basic research interest and existing and potential applications in many areas. The behaviour of magnetic nanostructures is particularly interesting when they are in contact with other dissimilar materials because their wavefunctions and/or magnetic fields extend considerably outside the physical structure. This makes them very susceptible to all types of proximity effects<sup>4</sup>.

For instance, when a ferromagnetic thin film (one in which the magnetic moments are all parallel) is in contact with an antiferromagnet (in which the magnetic moments are antiparallel), the interaction at the interface produces the so-called exchange bias. In an exchange-biased ferromagnet, the hysteresis loop is shifted so that it is no longer centred on zero field and the coercivity increases substantially<sup>5</sup>. (Coercivity is the size of the external field required to reverse the magnetization of a ferromagnet.) Thus the antiferromagnet provides an additional interaction at the interface, which in effect provides an additional magnetic anisotropy to help align the ferromagnetic moments in a certain direction. Because the antiferromagnet has no net bulk magnetization of its



**Figure 1** Beating the superparamagnetic limit for small magnetic nanoparticles. **a**, For very small ferromagnetic (FM) particles the magnetic anisotropy energy (responsible for keeping the magnetization oriented in certain directions) is comparable to the thermal energy ( $kT$ ). When this happens, the particles become superparamagnetic; as thermal fluctuations randomly flip the magnetization direction between parallel and antiparallel orientations. **b**, When the ferromagnetic nanoparticle is placed close to an antiferromagnetic (Anti-FM) surface the exchange bias interaction at the FM/Anti-FM interface provides additional anisotropy energy, which stabilizes the magnetization in one direction and prevents superparamagnetism.

own, it serves to pin (or stabilize) the magnetization of the ferromagnet without adding additional magnetization to the system.

Although the exchange-bias interaction has been widely studied and is currently used in computer read-heads and sensors, the underlying physical mechanism is not well understood. It was suggested previously<sup>6</sup> that the superparamagnetic effect in nanostructured magnets would be affected by exchange bias with an antiferromagnet, as shown in Fig. 1. With the ever-increasing demand for miniaturization, this would provide an avenue for "Beating the superparamagnetic limit", as Skumryev and co-workers<sup>3</sup> have now shown for cobalt (Co) nanoparticles.

In their work, Skumryev *et al.* compare the magnetic properties of Co nanomagnets confined in three dimensions, and which are embedded into paramagnetic ( $\text{Al}_2\text{O}_3$ ) or antiferromagnetic (CoO) matrices. For Co nanomagnets in the paramagnetic  $\text{Al}_2\text{O}_3$  matrix, they record a blocking temperature of 10 K, above which the particles are superparamagnetic.

However, Co nanomagnets of approximately the same size but surrounded by an antiferromagnetic CoO matrix have stable magnetic moments and do not become superparamagnetic up to 290 K, which corresponds roughly to the Néel temperature of bulk CoO. This is almost a 30-fold increase in the blocking temperature.

The authors interpret this increase as resulting from stabilization of the magnetic moment by the antiferromagnetic matrix — a conclusion that is supported by the shifted hysteresis loop of the sample cooled in an external field. Typically for exchange-biased systems, the quality of the Co–CoO interface may affect the exchange bias and change its magnetic remnance — the strength of the magnetization at zero external field after saturating the magnetization in high field — and coercivity. The interfacial quality can be improved by preparing particles with a CoO shell surrounding a Co core, before embedding them into the CoO matrix. In contrast with earlier experiments<sup>7</sup> on compacted core–shell (Co/CoO) particles, Skumryev and co-authors deposit alternating layers of core–shell nanoparticles and CoO layers to avoid complications arising from magnetic interparticle interactions. For the preparation of large arrays of monodisperse, well-separated core–shell (Co/CoO) nanoparticles, self-assembly techniques may offer greater control<sup>8</sup>.

These experiments show that the idea of using an antiferromagnet to “beat superparamagnetism” is valid, but much more work is required to understand the associated phenomena and to make them useful. Clearly, interfaces play a major role and therefore their understanding and control is important. Understanding how the additional exchange-bias stabilization influences magnetization relaxation times, and in turn the long-term stability, is also crucial for applications. Another challenge is to implement these ideas in device-friendly regular arrays — formed from monodisperse nanoparticles in two and three dimensions — in which coupling between the nanomagnets cannot be ignored. Understanding exchange bias in confined geometries and exploring the influence of different surface and interfacial anisotropies will also be essential. These are only a few of the important problems that must be studied, and will surely lead to new discoveries.

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## ZEOLITES

# Porous architectures

The porous structure of synthetic zeolites is key to their catalytic performance. A new germanosilicate with large interconnected channels of different sizes is capable of unique catalytic selectivity.

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**Z**eolites are strictly defined as crystalline microporous aluminosilicates that possess three-dimensional frameworks composed of tetrahedral units ( $\text{TO}_{4/2}$ , where T = Si or Al) linked through oxygen atoms. In contrast to activated carbon, activated alumina, or silica gel, the pores of zeolites have uniform sizes that are determined by their crystal structures. Because the size of the pore apertures is comparable to molecular dimensions (typically between 3 and 10 Å wide) zeolites can function as ‘molecular sieves’, excluding molecules larger than their pore windows.

Aluminium atoms in the framework introduce negative charges that must be counterbalanced by extra-framework cations. If such cations are hydrogen

ions then the zeolite is a solid acid and may function as a catalyst. In order to extend the catalytic applications of zeolites, a major research task both in industry and in academia is the synthesis of new zeolitic materials with ever more complex pore architectures. In this issue of *Nature Materials*, Avelino Corma and colleagues present a zeolite structure with large, interconnected pore channels<sup>1</sup>.

In practice, very few zeolitic materials meet the stringent definition given above. Trivalent atoms such as boron, gallium or iron may replace aluminium, and tetravalent atoms such as germanium and titanium may replace silicon. Even zinc, beryllium and lithium can occupy tetrahedral sites in certain zeolite structures. The use of these different elements during synthesis sometimes leads to materials with novel framework topologies or to materials with chemical and physical properties that are distinct from aluminosilicate analogues with identical frameworks. Although these materials possess framework atoms