

# **NANO-SCALE MAGNETISM**

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## Abstract

This paper presents an overview of the development, current status and future prospects for nano-scale magnetism. The natural progression from techniques for the preparation of bulk nano-scale magnets to the techniques of self-assembly and templating are discussed. The physics driving the technologically important nano-scale magnets is outlined, and areas where further study is required are highlighted. A number of areas for current or future application are also considered.

## Introduction

The generic discipline of nanotechnology is receiving considerable attention in the worldwide academic community at this time. Most major research centres have programmes in this area. This article will consider the sub-theme of nano-magnetism where research and development has been in progress for many years. Society already sees the benefits in terms of a range of products using such magnetic materials, and there is considerable potential for future developments.

In order to structure this overview for the general reader a number of subsections will be used. We will begin with an overview of key concepts in nano-magnetism, thereby defining a number of physical parameters which can be controlled by nano-materials engineering once the physics is elucidated. Three broad categories of nano-scale magnetic material can be defined. One is where the samples themselves are bulk, but where the technologically crucial parameters are dictated by structural features on the nanometre scale. These materials represent the nano-magnets currently commercially available, and where most of the basic science and property optimisation is well understood. Another category is where thin films of magnetic material are deposited such that one dimension at least is in the nanometre range. This is the area which is of great significance in such applications as data storage. The technically significant parameters are governed by the chemistry, geometry and separation of the layers. A further category can be made from those magnetic assemblies where patterning (using lithography) or self-assembly (using templating) are used to control the overall properties. The individual elements have properties dictated by the dimensions and element spacings. A final category is where the magnetic material is in the form of nano-particles. Nature has much to teach us here. For example, magneto-tactic

bacteria find the mud at the bottom of ponds with the aid of an embedded magnetic nano-particle and the local Earth's field vector.

## Key concepts in nano-scale magnetism

The field of nano-scale magnetism has yet to see definitive text books produced, but the text by O'Handley provides considerable useful background, and should be consulted by those less familiar with the language of magnetic materials [1]. There are also a number of recent reviews focussed on particular aspects of nano-magnetism which the reader might consult [2, 3, 4].

The materials considered in this article are all ferro- or ferri-magnetic at room temperature, and therefore demonstrate classic hysteresis loops under cyclic magnetic fields. Four key parameters of the hysteresis loop are influenced in nano-scale magnetic materials; the remanence, the coercivity, the permeability and the anisotropy.

Two forms of anisotropy need to be considered in further detail. It is generally true that in any magnet where there is a net magnetisation (the commonest being the fridge magnet), then there is an anisotropy associated with the physical dimensions of the sample. This anisotropy becomes dominant when one or more dimensions of the magnet are reduced to small length scales. In nano-scale magnets this anisotropy can dominate over intrinsic magneto-crystalline or magnetoelastic forms. It certainly cannot be ignored.

Until the discovery of nano-magnetic materials, little thought was given to the free surfaces of a sample, or to interfaces between different materials. At free surfaces atoms may relax away from their bulk co-ordination sites, and clearly the reduced number of nearest neighbours has an influence on the electronic structure at the surfaces. At interfaces there may be pseudo-epitaxy or dislocation networks which have their own effect on local electronic properties. The intrinsic magnetic anisotropy is directly related to the local electronic structure, and it has now been clearly shown that magnetic properties at surfaces and interfaces are significantly different to the bulk.

It is an electronic exchange interaction which leads to the alignment of the magnetic moments to give ferro- or ferri-magnetism. It is now known that it is possible to achieve exchange coupling between grains in a polycrystalline material, provided the grains are on the nano-metre scale, which can over-ride the

energetic demands of intrinsic magnetic anisotropies, and give long range magnetic alignment of atomic moments. This can significantly alter the parameters of the hysteresis loop discussed above.

We now go on to consider practical examples of nano-scale magnetic materials to exemplify these points.

### Bulk nano-scale magnets

The first reports of practical nano-scale magnets date back to 1938. Here an alloy of Fe with Al, Ni and Co (Alnico) was developed as a permanent magnet material. The spinodal decomposition of this alloy leads to long acicular magnetic grains of length 150nm and diameter 40nm. These grains can all be aligned if the decomposition takes place in the presence of a magnetic field. Shape anisotropy then dominates the magnetic properties, with the direction parallel to the long grain axis being the easy magnetic axis. A coercivity of 55kA/m and remanence of 1.3T is typical for these rather low grade materials.

In the 1970s there was much research in to the use of rapid solidification for the extension of solubility ranges in alloys. Serendipitously this led to the discovery of amorphous ferromagnetic metals. Studies in to the thermal stability and devitrification of these materials led on to the discovery of alloys with a grain structure on the nano-metre scale.

Currently the best soft magnetic materials (low coercivity, high permeability, low anisotropy) are alloys based on the archetype material  $\text{Fe}_{73.5}\text{B}_9\text{Si}_{13.5}\text{Nb}_3\text{Cu}_1$ , known by the name FINEMET®. The Nb enhances the rate of crystal nucleation, whilst the Cu retards crystal growth. This results, by suitable choice of annealing time and temperature, in a material with bcc- $\text{Fe}_3\text{Si}$  grains of size 10-20nm embedded in an amorphous ferromagnetic matrix. The resulting competition between ferromagnetic exchange and the intrinsic magnetic anisotropy allows the exchange length to encompass many grains. A coercivity as low as 0.3A/m has been achieved by this technique. This topic has been well reviewed by Herzer [5].

It is a clear demonstration of the subtlety of the basic physics in nano-scale magnetism that a simple change of composition can take us from the softest ferromagnets currently available, to the hardest. By the same route of rapid solidification in to an amorphous phase, and subsequent devitrification, alloys based on  $\text{Nd}_2\text{Fe}_{14}\text{B}$  can achieve very high coercivities and remanence – the essential features of a

permanent magnet. If the alloy is made Fe-rich then exchange coupling gives remanence enhancement, and if the alloy is Nd-rich then the coercivity is enhanced. This ability to tailor the overall properties has been commercially exploited to produce magnets for light weight, low volume and high efficiency motors and drives. Good examples are the motor and miniature headphones in a personal stereo system, portable power tools and the continued moves to all-electric means of transportation. These permanent magnet materials have been reviewed by Skomski and Coey [6].

### Thin film nano-magnetism

The developments in this area have been driven by the demands of the data storage industry. The compound growth rate (cgr) for areal density on a disk has risen at more than 100%p.a. in recent years. It is not untypical to use a 120Gb hard drive in a middle range desktop computer, and there have been recent announcements of 100Gb/in<sup>2</sup> densities on conventional media. This is an effective size per bit which is sub micrometer.

There are basically three ways of storing the data on a magnetic recording medium. In the longitudinal case acicular particles are placed with their long axis parallel to the read/write direction, in the normal case the long axis of the particles is perpendicular to the read/write direction but still in the plane of the medium. In the perpendicular case the long axis is normal to the media surface, but the read/write direction is still in plane. This last option offers the potential for the highest densities provided the individual particle coercivity is sufficiently high to avoid switching.

The grain size of magnetic particles cannot be reduced indefinitely without affecting the magnetic properties. Below a certain critical size for a given material, the remanent magnetisation is no longer fixed in direction by anisotropy, but may be flipped by thermal energy. This is the so-called super-paramagnetic limit. For an anisotropy energy density of 105Jm<sup>-3</sup>, the super-paramagnetic radii for stability are 7nm for 1 year and 5nm for 1s. We will consider other options in the next section.

The decrease in the physical bit size also places stringent demands on the read/write head. The write field must have the same lateral scale as the required bit to be written. This has been achieved by using multilayer structures. In the current “spin-valve” technology for read heads, four layers are used as the

active parts [2]. A permanent magnet bias layer (e.g. IrMn) is adjacent to a soft ferromagnetic layer such as NiFe (the pinned layer). This, in turn, is spaced a critical distance away from a second NiFe layer (the free layer) by a metallic but non-magnetic layer such as Cr or Cu. The free layer is free to rotate its magnetisation under the influence of stray fields from the bits in the media. If the free and pinned layer magnetisations are parallel, both spin channels are free to conduct and the resistance is low. If the free and pinned layer magnetisations are anti-parallel then neither spin-channel is free to conduct without significant scattering, and the resistance is high. This gives a device with two states, high and low resistance, suitable for digital data applications. The thickness of each layer and the spacing between the NiFe layers are all a few nanometres and must be tightly controlled.

It has recently been seen that the NiFe layers, chosen for their low anisotropy and magnetostriction, show properties different to the bulk at these thicknesses, and work is in progress to understand the physics of this process and hence find methods of controlling this potential source of degradation in device performance [7].

A step on from the bulk permanent magnet materials is work on NdFeB thin films for use in microelectromechanical systems (MEMS). Careful control of the fabrication can lead to films with very promising magnetic properties [8]. Here, the process of film production allows control of the macroscopic texture, and thus the overall magnetic properties. Maximum energy products close to  $200\text{kJm}^{-3}$  have been achieved.

### Self assembled and lithographically produced nano-magnets

The work on bulk nano-magnets discussed above demonstrates very clearly that tight control over the size, orientation, spacing and inter-particle phase can lead to novel magnetic properties. The techniques of self-assembly lend themselves to trying ways of overcoming the limitations of bulk processing in order to create designer materials.

Templating can be used to create regular arrays of wires in a host matrix [9]. It is possible to produce nanometre diameter channels in the polymer which can then be filled with magnetic material by electrodeposition. The net properties reflect the inter-wire interactions and the geometrical arrangement of

the wires. Considerable work remains to be done in terms of controlling the size and spacing of the wires, and also in determining the maximum area which can be produced for the array before defect structures come in. In principle, this is a serious route for the production of next generation recording media.

A recent report has demonstrated the successful self-assembly of FePt nano-particles in to monolayer, sub-monolayer and multilayer rings [10]. A number of magnetic configurations were achieved.

The best permanent magnet materials (highest energy product at over  $450\text{kJm}^{-3}$ ) at present are the Fe-rich NdFeB bulk magnets discussed above. It is an obvious step to try and produce the template of hard magnetic grain with soft magnetic grains surrounding it by a self assembly technique. A promising start has been made using FePt nano-particles as the hard grain, and  $\text{Fe}_3\text{O}_4$  as the soft grain, to produce exchange coupled nano-composites using self-assembly [11]. The best maximum energy product is around  $160\text{kJm}^{-3}$ , already close to half that of the best bulk material.

### The research environment

It is clear from the discussion above that studies in nano-scale magnetism require a highly interdisciplinary environment. The subject demands the attention of physicists, chemists and materials scientists. There remain many challenges to be faced in terms of understanding the fundamental science, as well as finding good routes to applications. Undoubtedly this will be an active and fruitful area for many years to come.

The interdisciplinarity required does present challenges in terms of knowledge and skills transfer. The scientific journals will also have to find ways to publish papers that reflect this high degree of interdisciplinarity. A significant step in this direction will be taken in a forthcoming issue of J.Phys.D: Applied Physics (2003), where three review articles will appear from backgrounds not normally covered by that journal. This should stimulate studies in nano-scale magnetism, and set a useful precedent for the future [12,13,14].

### Conclusions

This article has set out the case that the magnetics community is already very well established in terms of bulk nanomagnetic materials. These materials, both magnetically hard and magnetically soft, are already



seeing technology pull-through for efficiency and weight gains. The data storage industry is actively working in nanostructures in order to satisfy the demand for increases in data storage density. The future for fabricated nanostructures or magnetic nanoparticles has possibilities on many fronts. The key is to enable interdisciplinary activity across a far wider front than perhaps has ever existed previously.

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## References

1. O'Handley, R.C. (2000) *Modern Magnetic Materials: Principles and Applications*, New York, Wiley-Interscience.
2. Nogués, J. and Schuller, I.K. (1999) Exchange bias. *J.Magn.Magn.Mat.* **192** 203-232
3. Martín, J.I., Nogués, J., Liu, K., Vicent, J.L. and Schuller, I.K. (2003). Ordered magnetic nanostructures: fabrication and properties. *J.Magn.Magn.Mat.* **256** 449-501.
4. Skomski, R. (2003). Nanomagnetism. *J.Phys.: Condens. Matter* **15** R841-R896
5. Herzer, G. (1990) Grain size dependence of coercivity and permeability in nanocrystalline ferromagnets. *IEEE Trans. Mag.* **26** (5), 1397-1402.
6. Skomski, R. and Coey, J.M.D. (1999) *Permanent Magnetism*, Bristol, IoP Publishing.
7. Hollingworth, M.P., Gibbs, M.R.J. and Hill, E.W. (2003) Surface, interface and bulk studies of NiFe nanometre films for magneto resistive heads. *J.Appl.Phys.* **93** (10) 8737-8739.
8. Castaldi, L., Gibbs, M.R.J. and Davies, H.A. (2003) Deposition of hard magnetic rare-earth-Fe-B thin films by magnetron sputtering. *J.Appl.Phys.* **93** (11) 9165-9169.
9. Thurn-Albrecht, T., Schotter, J., Kästle, G.A., Emley, N., Shibauchi, T., Krusin-Elbaum, L., Guarini, K., Black, C.T., Touminen, M.T. and Russell, T.P. (2000). Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates. *Science* **290** 2126-2129.

10. Zhou, W., Fang, J., He, J., Stokes, K.L and O'Connor, C.J. (2003) Self-assembly FePt nanoparticles into ring structures. *J.Appl.Phys.* **93** 7340-7342.
11. Zeng, H., Li, J., Liu, J.P., Wang, Z.L. and Sun, S. (2002) Exchange-coupled nanocomposite magnets by nanoparticle self-assembly. *Nature* **420** 395-398.
12. Pankhurst, Q.A., Connelly, J., Jones, S.K. and Dobson, J. (2003) Application of magnetic nanoparticles in biomedicine”, *J.Phys.D: Applied Physics* *in press*.
13. Tartaj, P., Morales, M.P., Veintemillas-Verdaguer, S., Gonzalez-Carreno, T. and Serna, C.J. (2003) The preparation of magnetic nanoparticles for application in biomedicine *J.Phys.D: Applied Physics* *in press*
14. Berry, C.J. and Curtis, A. (2003) Functionalisation of magnetic nanoparticles for application in biomedicine *J.Phys.D: Applied Physics* *in press*