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"Introduction" to *Advanced Magnetic Nanostructures*

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Chapter 1

INTRODUCTION

The nanostructures considered in this book are magnetic and characterized by *structural* length scales ranging from a few interatomic distances to about one micrometer. The basic length unit is the *nanometer* (1 nm = 10^{-3} μm = 10^{-9} m), corresponding to about four interatomic Fe-Fe distances. Magnetic nanostructures pose experimental challenges, exhibit interesting physical phenomena, and have many present or potential applications. An important aspect is that structural lengths affect, but only partly determine, the magnetic length scales encountered in the structures. Examples are domains in semihard nanoparticles, where both the domain size and the domain-wall thickness may be smaller than the particle size, and polycrystalline soft-magnetic nanostructures, where the magnetic correlation length is much larger than the crystallite size.

Due to rapid progress in the fabrication and processing of nanostructures, it is now possible to realize a broad variety of geometries, crystalline textures, and chemistries. For a given geometry, the structures can be fabricated using a variety of magnetic materials (compounds), with different local magnetic properties and crystalline textures. The Appendix presents some magnetic materials of interest in nanomagnetism.

1. BASIC DEFINITIONS AND UNITS

The magnetic moment **m** of the atoms in a nanostructure nearly exclusively originates from the electrons in the partially filled inner shells of transition or rare-earth metals. There are both spin (S) and orbital (L) contributions, but since L is much smaller than S in most iron-series transition-metal magnets, the magnetic moment is often equated with the spin polarization. The situation is similar to that encountered in bulk magnets, although both S and L may be modified at surfaces and interfaces (Ch. 2). As in infinite solids, nuclear moments are much smaller than electron moments and can be ignored safely for most applications.

The magnetic moment of an atom is created by intra-atomic or Hund's-rules exchange, which favors parallel spin alignment on an atomic scale. In addition, ferromagnetism requires *interatomic* exchange, to ensure parallel alignment of the moments of neighboring atoms. The resulting net moment gives rise to the magnetization $\mathbf{M} = \mathbf{J}/\mu_0$ which is defined as the moment per unit

volume. In bulk ferromagnets, the competition between interatomic exchange and thermal disorder leads to the vanishing of the spontaneous magnetization $M_S = |\mathbf{M(r)}|$ at a well-defined sharp Curie temperature T_C. However, the existence of a Curie-point singularity is limited to infinite bodies, and in nanostructures, the concepts of magnetic phase transitions must be reevaluated (Ch. 3).

Spin-orbit coupling in combination with local crystal-field interactions gives rise to magnetic anisotropy. In the simplest case, magnetic anisotropy is of the uniaxial type and described by the lowest-order anisotropy constant K_1. This constant is equal to the energy density necessary to turn the magnetization from the easy to a hard magnetization axis. In addition, there are shape-anisotropy contributions of magnetostatic origin. In nanostructures, surface, interface, and shape anisotropy contributions are often important, particularly in cubic materials, where the lowest-order bulk anisotropy is zero.

An applied magnetic field **H** changes the magnetization by rotating the local moment. Since the magnetic anisotropy yields energy barriers between different magnetization states or spin configurations **M(r)**, the field dependence of the net magnetization exhibits *hysteresis.* Important hysteretic properties are remanence M_r, defined as the zero-field magnetization after saturation in a strong magnetic field, and the coercivity H_c. The latter is defined as the reverse magnetic field at which the volume-averaged magnetization of an initially saturated magnet reaches zero. Some other hysteretic properties of specific nanostructuring offers many tools to tune hysteretic properties. For example, the coercivity of advanced magnetic nanostructures varies from about 1 μT to several T. Analytical and numerical aspects of the hysteresis of magnetic nanostructures will be treated in Chs. 3 and 4, respectively.

The structural length scales of nanomagnets are intermediate between interatomic and macroscopic distances, but nanomagnetism cannot be reduced to a mixture of atomic-scale and macroscopic phenomena. For example, most extrinsic properties are realized on a nanoscale, and nanostructuring is used to produce optimized hard, soft, information-storage and sensor materials. A dynamic aspect of this interplay between atomic (or intrinsic) and hysteretic (or extrinsic) phenomena is that equilibration times vary from less than 1 ns to millions of years. This determines, for example, the magnetic switching time of spin-electronics structures and the lifetime of information stored in magnetic recording media. This is related to the thermal instability of the magnetization direction known as superparamagnetism (Bean and Livingston 1959). This effect occurs in very small particles and is strongly temperature dependent (Ch. 3).

In this book, the preferred *length unit* is 1 nm (10^{-9} m), but 1 Å = 0.1 and 1 μm = 1000 nm are also used, particularly for submicron features having

sizes of several 100 nm. Recording densities are also measured in bytes per square inch or bytes per square centimeter (1 in^{-2} = 6.452 cm^{-2}). Both SI and Gaussian units will be used for *magnetic quantities,* with explicit conversions occasionally included in square brackets. This also includes the parallel or alternate use of the SI unit tesla for coercivity and magnetization, as compared to the correct but cumbersome unit A/m. The latter corresponds to $B = \mu_o(M + H)$, and the former is obtained by incorporating μ_o into M and H, so that one actually considers $\mu_o M$ and $\mu_o H$. In the Gaussian system, multiplying the magnetization (emu/cm^3) by the dimensionless number 4π changes the unit to gauss. (This is similar to measuring the perimeter of an island in miles and its diameter in feet.) Some everyday numerical *conversion rules* are: (i) 1 T = 10 kOe ≈ 0.8 MA/m (coercivity), (ii) 1 emu/cm^3 = 1 kA/m and 1 T = 10 kG ≈ 0.8 MA/m (magnetization), (iii) 1 T^2 = 100 MGOe ≈ 800 kJ/m^3 (energy product). Finally, an SI susceptibility of 1 corresponds to a Gaussian susceptibility of 4π. In the above conversions, we have used the numerical relation that $10/4\pi = 0.7958 \approx 0.8$.

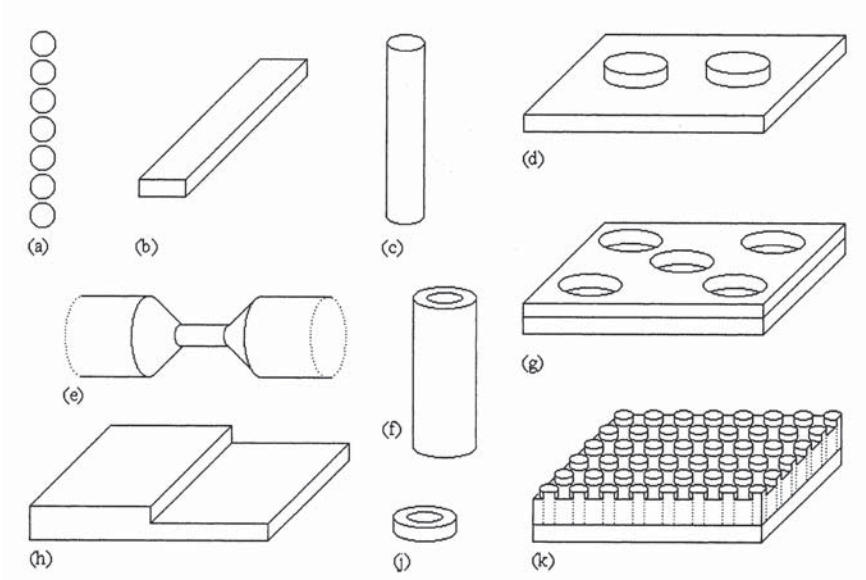

Figure 1. Typical nanostructure geometries: (a) chain of fine particles, (b) striped nanowire, (c) cylindrical nanowire, (d) nanodots, (e) nanojunction, (f) nanotube, (g) antidots, (h) vicinal surface step, (j) nanoring, and (k) patterned thin film. Note that the figures can consist of multilayered and granular nanocomposites.

2. MAGNETIC NANOSTRUCTURES

Magnetic nanostructures can be produced in a wide range of geometries. Figure 1 shows some examples. In combination with specific choices of magnetic materials for the structures—or for parts of the structures—this versatility is a major reason for interest in magnetic nanostructures. Several chapters of this book deal with the fabrication, investigation, and application of individual geometries, such as nanowires and patterned thin films. The following paragraphs briefly characterize typical geometries, mention some systems of practical or scientific interest, and provide links to the individual chapters of this book. (For references, see the Chapters 2 to 15 and the further-reading section below.)

2.1. Nanoparticles, Clusters, and Molecular Magnets

Small magnetic particles exist in nature or are produced artificially (Chs. 6 to 8). Nanoparticles have sizes ranging from a few nanometers to submicron dimensions (Ch. 7), whereas molecular magnets (Ch. 6) contain a few magnetic atoms in well-defined atomic environments. Clusters are intermediate structures, with less well-defined atomic environments but exhibiting atomic features such as facets (Ch. 8).

Examples of naturally occurring nanoparticles are magnetite (Fe_3O_4) nanoparticles precipitated in bacteria, insects and higher animals, and magnetite and other oxide particles responsible for rock magnetism. Nanobiomagnetics is concerned not only with questions such as the role of magnetite particles for horizontal and vertical orientation of animals but also with important medical issues, such as local drug administration and cancer diagnosis (Ch. 15). The small remanent magnetization of magnetic rocks, first analyzed by Neel in the 1940's, is exploited, for example, in archeomagnetic dating and to monitor changes in the Earth's magnetic field. Small oxide particles, less than 10 nm in diameter, are observed in gels having the nominal composition $FeO(OH)\cdot nH_2O$. Fine particles are also encountered in meteorites.

Some artificially produced magnetic nanoparticle structures are Fe in Al_2O_3 and so-called "elongated single-domain particles." Interesting applications of small particles are stable colloidal suspensions known *ferrofluids. A* variety of materials can be used, such as Fe_3O_4, $BaFe_{12}O_{19}$, Fe, Co, and Ni, and a typical particle size is 10 nm. Most ferrofluids are based on hydrocarbons or other organic liquids, whereas water-based ferrofluids are more difficult to produce. They are used as liquids in bearings and to monitor magnetic fields and domain configurations.

2.2. Granular Nanostructures

Embedded clusters, granular materials, and other bulk nanostructures are of great importance in nanoscience. The structural correlation lengths of typical nanocomposite materials range from about 1 nm in x-ray amorphous structures to several 100 nanometers in submicron structures. Magnetic glasses and atomic-scale defect structures are beyond the scope of nanomagnetics, but they are of indirect interest as limiting cases and because nanomagnetic phenomena have their quantum-mechanical origin in atomic-scale magnetism.

Depending on grain size and microchemistry, granular nanostructures are used for example as permanent magnets (Nd-Fe-B), soft magnets (Fe-Cu-Nb-Si-B), and magnetoresistive materials (Co-Ag). There are two types of exchange-coupled permanent magnets: isotropic magnets, which exhibit random anisotropy and remanence enhancement, and oriented hard-soft composites, which utilize exchange coupling of a soft phase with a high magnetization to a hard skeleton.

Closely related systems with many potential applications are magnetic clusters deposited in a matrix. For example, the narrow size distribution of 10–20% makes this material interesting as a granular media for magnetic recording. A well-known *soft-magnetic* nanocomposite is the "Yoshizawa" alloy $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$, which consists of DO_3-structured Fe_3Si grains embedded in an amorphous matrix.

2.3. Particle Arrays and Functional Components

Two-dimensional arrays of nanoparticles are of interest as scientific model systems and have many present or future applications. For example, advanced magnetic recording media can be characterized as a complex array of magnetic particles, and interest in dot arrays has been sparked by the search for ever-increasing storage densities in magnetic recording. In very small dots, quantum-mechanical effects are no longer negligible, and there are phenomena such as quantum-well states. These effects are of interest in quantum computing and spin electronics.

Most easily produced and investigated are submicron dots made from iron-series transition metals, such as Ni, but it is also possible to use metallic alloys, such as Permalloy, and to reduce the dot size to less than 100 nm. The dots may form square or hexagonal arrays, or structures such as corrals. Among the investigated phenomena are the properties of individual dots and interdot interactions. A related class of nanostructures are *antidots,* that is, holes in a film rather than dots on a film. Potential applications include magnetic recording, sensors, magnetic and quantum computing, micron- and submicron-size mechanical devices, short-wavelength optics, and spin elec-

tronics. Other "functional" building blocks are, for example, nanojunctions, spin valves, and tips for magnetic-force microscopy (MFM tips).

2.4. Nanowires

There is a smooth transition from elongated dots and thin-film patches to nanowires. Magnetic nanowires have present or potential applications in many areas of advanced nanotechnology, including patterned magnetic media, magnetic devices, and materials for microwave technology. There a various methods to produce nanowires, such as deposition on vicinal surfaces and electrodeposition, including electrodeposition into porous alumina templates (Section 3).

Much of the early work on magnetic nanowire arrays was concerned with exploratory issues, such as establishing an easy axis for typical preparation conditions, the essential involvement of shape anisotropy, as opposed to magnetocrystalline anisotropy, and the description of magnetostatic interactions between wires. More recently, attention has shifted towards the understanding of magnetization processes, such as the transition from curling-type to quasi-coherent nucleation, the influence of deposition-dependent polycrystallinity of typical transition-metal nanowires. Some other interesting phenomena are magnetic-mode localization, as evident *e.g.* from experimental activation volumes, spin-waves, and current-induced magnetization reversal.

2.5. Magnetic Thin Films and Multilayers

Magnetic thin films and multilayers can be classified as magnetic nano-structures, too, but it is common to treat homogeneous thin films and multilayers as a separate branch of magnetism, intermediate between nano-magnetism and surface magnetism. However, many recently developed and investigated nanostructures are thin-film nanostructures. Examples are self-assembled thin-film nanostructures (Ch. 9), patterned nanomagnetic thin films (Ch. 10), hard-magnetic thin-film nanostructures and thin films for magnetic recording (Ch. 11).

Semihard thin films are used in magnetic recording media and have, more recently, attracted attention as tools for magnetic information processing. In addition, on a length scale of a few interatomic distances, there is a variety of interesting thin-film effects, such as vicinal and interface anisotropies, moment modifications at surfaces and interfaces, thickness-dependent domain-wall and coercive phenomena, interlayer exchange-coupling, and finite-temperature magnetic ordering. A specific example is the nanoscale exchange-coupling or "exchange-spring" effects in multilayers.

3. FABRICATION AND CHARACTERIZATION

The broad variety of magnetic nanostructures corresponds to a diverse range of processing methods. The suitability of individual methods depends on the length scale and geometry of the nanostructures. In addition, each method is usually restricted to a relatively narrow class of magnetic materials.

Granular nanostructures are produced by methods such as mechanical alloying and chemical reactions. A traditional though somewhat cumbersome method to fabricate *nanoscale particle arrays* of magnetic, dots, and wires on thin films is nanolithography. Other examples are molecular-beam epitaxy, the use of STMs, and chemical vapor deposition. The call for well-characterized large-area arrays of nanoparticles has stimulated the search for advanced production methods such as laser-interference lithography (LIL), where laser-intensity maxima effect a local transformation of a nonferromagnetic material into ferromagnetic islands. Another development is the use of focused ion-beam milling (FIB) to create small particles and particle arrays with well-defined properties.

Thin-film *nanowires* are comparatively easily obtained by depositing magnetic materials on vicinal surfaces and by exploiting structural anisotropies of the substrate. They can be produced with thicknesses down to one or two monolayers. Electrodeposition of magnetic materials into porous alumina may be used to produce regular wire arrays (see Sellmyer *et al.* 2001 and references therein). Other ways of fabricating cylindrical nanowires include deposition into molecular sieves, track-etched polymer membranes, and mica templates. By electrodeposition into porous anodic alumina it is now possible to produce hexagonal Fe, Co, and Ni nanowire arrays with diameters ranging from 4 to 200 nm, and lengths of up to about 1 μm, and variable center-to-center spacings of the order of 50 nm. The resulting materials are of interest as magnetic recording media, for optical and microwave applications, and as electroluminescent display devices. Aside from the above-mentioned iron-series transition-metal elements, there is interest in depositing alloys and multilayers, such as Fe/Pt, into porous templates.

The structural and magnetic characterization of magnetic nanostructures is the main focus of Ch. 5 and of various sections and subsections throughout the book. Structural correlation lengths can be probed for example by X-ray diffraction, small-angle neutron scattering (SANS) and electron microscopy. Magnetic measurements are performed with the methods known from bulk and surface magnetism, although some techniques must be adjusted to the small signals from certain structures. Examples are vibrating sample magnetometry (VSM), magneto-optical Kerr effect (MOKE) measurements, and

SQUID magnetometry. Some methods, such as magnetic-force magnetometry, are nanospecific and presently being applied to measure hysteresis loops of nanoscale magnetic particles.

4. APPLICATIONS

Magnetic nanostructures are used in the form of traditional magnetic materials, such as hard and soft magnets, and in specific functional structures, such as sensors. Hard or *permanent magnets* are used, for example, in electromotors, hard-disk drives, loudspeakers, windshield wipers, locks, refrigerator magnets, and microphones. Some applications, such as toys, do not usually require high-performance magnets, but hard-disk drives and other high-tech applications require highly sophisticated rare-earth permanent magnets with well-defined nanostructures (Ch. 12). Compared to the highly anisotropic hard magnets, *soft magnets* exhibit very low magnetic anisotropy. They are widely used for flux guidance in permanent-magnet and other systems, in transformer cores, and for high-frequency and microwave applications, and in recording heads. In advanced soft-magnetic materials, nanostructuring is used to reduce magnetic losses by controlling anisotropy, eddy-current losses, and other properties (Ch. 13).

A key application and driving force of magnetic nanotechnology is *magnetic recording media.* They are used not only for audio-visual technology, for example in audio and video tapes, but also in computer technology, for example in hard-disks (Ch. 11). A remarkable increase in areal density of many orders of magnitude in the last two decades has relied heavily on nanostructuring of media and read and write heads.

Artificial nanostructuring is a way of creating completely new technologies. One area is spin electronics, and various types of nanostructures, such as multilayers and nanojunctions, are being used or investigated in this context (Ch. 14). The magnetoresistance of metallic thin films, granular nanostructures and magnetic oxides are exploited in sensors, and a problem of current interest is spin injection into nonferromagnetic metals and magnetic semiconductors. Other recent developments are magnetic nanostructures for quantum computing, multiferroics (where nanoscale effects are exploited to synergize electric and magnetic degrees of freedom), and nanoparticle ferrofluids for cancer treatment, guided by a magnet and delivering high local doses of drugs or radiation. Nanoscale effects are also exploited in micro-electromechanical systems (MEMS) and magnetic-force nanotips made from CoPt.

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