

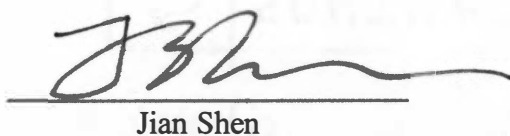
To the Graduate Council:

I am submitting herewith a dissertation written by John Philip Pierce entitled "Tailored Magnetic Nanostructures on Surfaces." I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a major in Physics.

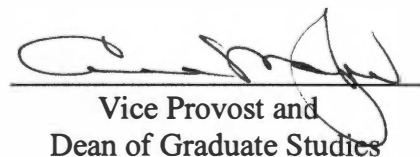


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Tailored Magnetic Nanostructures on Surfaces

A Dissertation

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Degree

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Dedication

In memory of my Uncle Chuck and my Grandpa Pierce.

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I've always looked forward to writing this part. As it turns out, this moment is more fun than I imagined because so many wonderful people have helped me along the way. To everyone that I will mention here: I hope this finds you well and makes you smile.

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Walters. I can't wait to see what Art puts on my surface group plaque on the day that I am "Big Edded." John Wendelken has always been just as willing to share his wisdom, and is one of the most pleasant people to be around that I have met. I'll miss his lunchtime stories about life in Germany, "Tennessee go-fasters", etc. Dr. Zehner always cared about my progress. He made sure that I avoided "pilot error" and felt a sense of "ownership" for the equipment. Gareth, Lars, and Zheng Gai were great people to work with and have been even better friends. Vicki Barnes, Gary Ownby, Phil Herrell, Dave Bowling, and Wayne Bullard all deserve thanks for helping me along the way.

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on the field and, more importantly, at the beer cooler. Under No-Hit's management and despite his third base coaching ("Whaddaya mean? Nobody listens to me!"), we took the first tournament championship in the 26-year history of Stonefinger softball. How sweet it was. Wednesday night basketball with Jerry, Bill, and a handful of Stonefingers was great. We'd play two or three games and then head off to the Buffalo Grille where Rich or Celeste would pour the coldest Guinness in town. And no matter how cold, rainy, or snowy it was at 10am on winter Sundays, the best place to be was outside on the football field with the same group.

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Abstract

Nanostructuring has introduced us to a new world of tunable, artificially structured materials. An exciting aspect of this new world is that *we control* where the atoms, or layers of atoms, are arranged in materials and have learned that this can awaken new properties in them. But, we are only at the beginning stages in developing this control and an understanding of what can be done with it. This dissertation is about an important part of finding our way in this new world; learning to tailor magnetic nanostructures on surfaces. We begin by showing ways in which the magnetic properties of ultrathin films, nanostripes, and isolated nanoclusters can be systematically varied in order to teach us about their behavior. The ultrathin films are from the historically challenging Fe/Cu(100) system. We use small fractions of a single layer of cobalt capping atoms to control their magnetization direction and find a completely new way to cause the magnetization direction to reorient. The nanostripes are made of alloys of iron and cobalt on a tungsten surface. We explore how the magnetic ordering in these stripes is affected by variation of their composition. We then show how changing the size and spacing of isolated Fe dots on a copper surface can teach us about magnetic interactions between them. Finally, we show how our ability to synthesize the dots represented the last piece in an important puzzle. This work enables us to make the first direct observation of how the magnetic properties of a particular amount of a single material change as it is prepared in the form of an ultrathin film, wire array, or dot assembly on a common template.

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Chapter 1

Introduction to Magnetic Nanostructures

1.1 The fountain of youth for a mature field of study.

Magnetic materials have served mankind for nearly two thousand years. A manuscript from the Han dynasty in China from 83 AD references a “south-pointing spoon” made from a curious material [1]. This, of course, was the precursor to the compass, which is believed to have been in widespread use on Chinese ships eight centuries later and became known to Europeans sometime during the 1100’s.

A crude understanding developed when it was realized that elongated pieces of the special material that could be used in compasses always had two magnetically distinguishable ends, or “poles”. The north-seeking pole of one piece was always repelled by (attracted to) the north-seeking (south-seeking) pole of another piece. This “dipole interaction” is one of the most basic interactions found in magnetic materials, and can explain, as shown in Fig. 1.1, how the compass works and why parents are able to hang their children's report cards on their refrigerators.

In Denmark in 1819, Hans Christian Oersted noticed that passing an electric current through a wire affected the direction of the needle of a compass that was placed nearby [2]. This is the first documented observation of the intimate relationship between electric currents and magnetic fields that was later described formally by the Law of Biot and Savart and Ampere's Law. The main consequence

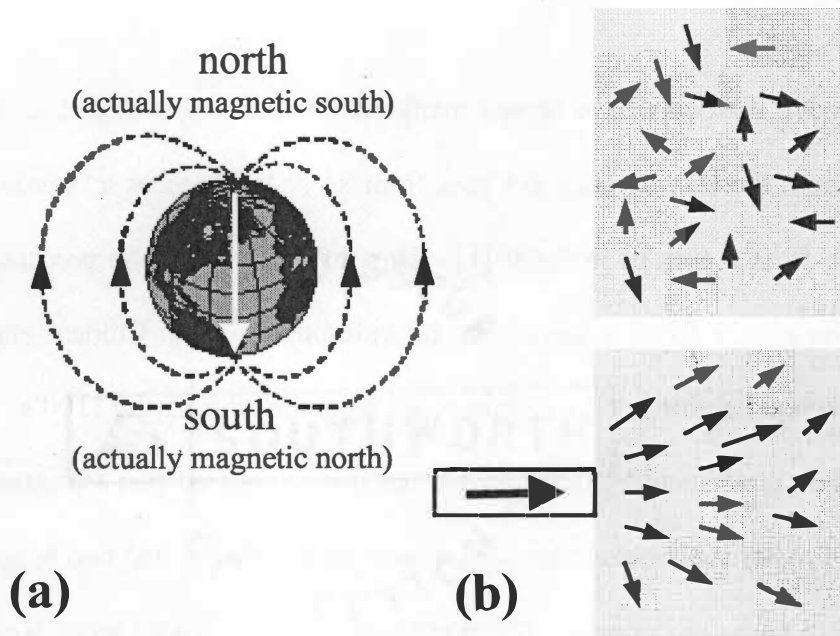


Figure 1.1: Two common ways in which people experience the dipole-dipole interaction. (a) The earth's magnetic field (dotted lines) can be roughly thought of as being due to a magnetic dipole (white arrow). The needle of a compass held by a traveler on the earth's surface tends to point along the field lines in the direction indicated by the dark arrowheads. (b) A chunk of the metal from a refrigerator door has clusters of iron-containing compounds that behave like tiny, randomly oriented magnetic dipoles. When a magnet is brought near the surface of the refrigerator, the dipoles re-orient so that their south-seeking ends point toward the north-seeking end of the magnet. The attractive force between dipoles that are in this configuration is usually strong enough to pin a drawing or report card in between.

of these Laws is that magnetic fields can produce currents and that currents produce magnetic fields.

This interplay is useful, and is exploited beautifully in "read/write heads" that are used for recording and playback in modern devices such as cassette recorders and VCRs. A simple schematic of one of these devices is shown in Fig. 1.2(a). When operating in the "write" mode, current pulses produce magnetic field pulses in the magnetic material and in the gap between the pole pieces. These field pulses force the dipoles in a chunk of the magnetic recording medium (a cassette or VCR tape) to align in particular directions, as shown in the figure. In this way, information is stored in magnetic blocks, or "bits" on the tape. When operating in the "read" mode, advancing the tape moves the magnetic bits past the gap, producing changing magnetic fields that lead to current in the pickup coil. Figure 1.2(b) shows how four of these read heads (only two are visible) are combined in a typical VCR. Audio cassette recorders and VCRs are relatively modern devices, but are based upon physics that has been understood for centuries.

It would seem that we have mastered the use of magnetic materials. We've just seen that our knowledge of dipoles and of the interplay between magnetic materials, fields, and currents has led to the development of devices that range in complexity from refrigerator magnets and compasses to motors and information storage/playback devices. Despite the apparent maturity of the field, the last 15 years have seen a sudden and drastic return to prominence of the study of magnetism and magnetic materials. This excitement comes from our recent progress in creating and

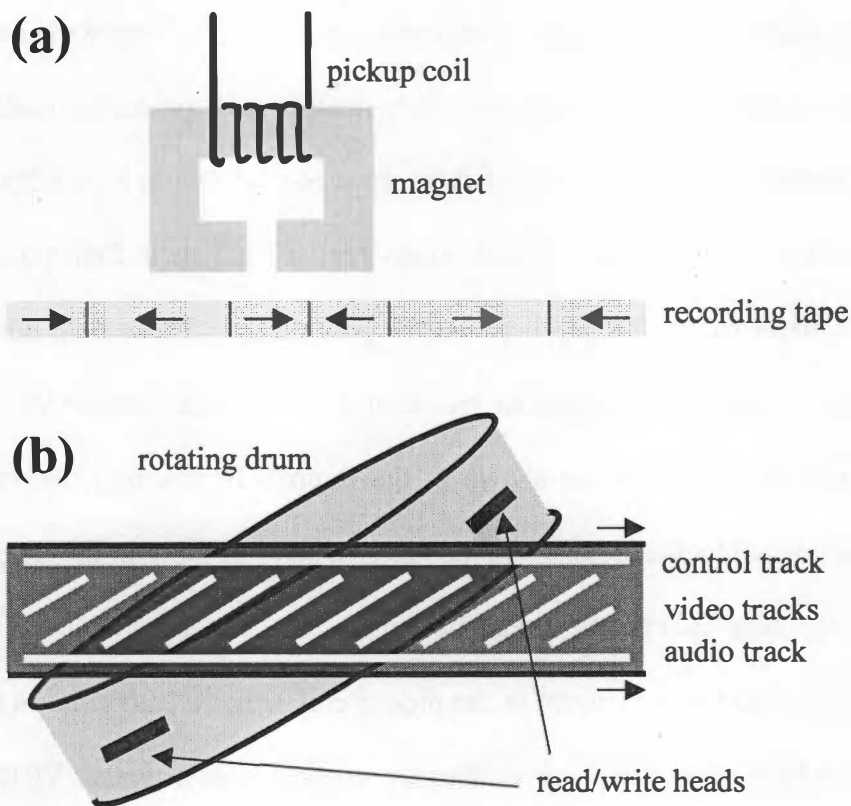


Figure 1.2: Modern applications of dipoles and the interaction between magnetic fields and current. (a) A typical read/write head, as found in an audio cassette recorder. When operating in the write mode, information is sent to the pickup coil in the form of current pulses. These current pulses lead to magnetic field pulses in the gap of the magnet. Magnetic dipoles in the tape respond to these field pulses, and store a historical record of them. In the read mode, the changing magnetic fields produced by the moving tape are converted to changing currents in the pickup coil, which can be sent to a loudspeaker. (b) A typical video-cassette recorder (VCR) has four of the read heads from (a) mounted on a rotating drum. (Only two heads are visible here.) To save space and reduce the reel speed of the tape, the video information is written on the tape diagonally, in 0.04 mm wide stripes or "tracks". When it is playing, the videotape advances (to the right in the figure) at a rate of 1.31 inches per second and the drum rotates 30 times per second [3]. The relative speed of the read heads and the videotape is 25 miles per hour!

characterizing magnetic structures on the nanometer size scale. Why is this? *Don't nanoscale structures behave like smaller versions of macroscopic objects?*

In the sections that follow, we will answer the first question and find out that the answer to the second question is “absolutely not!” In a 1959 lecture entitled *There's Plenty of Room at the Bottom*, Richard Feynman pointed out that since the research of his time dealt with structures and techniques that characterized on length scales much larger than that of the atom, there would be a tremendous amount of excitement as scientists learned to focus on nanoscale phenomena. Feynman anticipated the birth of a whole new field that would be “not quite the same as the others in that it will not tell us much of fundamental physics (in the sense of, “What are the strange particles?”) but... more like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations [4].” As we will see, it has turned out to be at least as exciting as he imagined.

1.2 Why does anyone care about magnetic nanostructures?

“What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances can have, and of different things that we can do.” [4]

- Richard Feynman, December 29, 1959.

In this section, we discuss the reasons for the excitement and activity in the study of nanostructured magnetic materials. As Feynman foresaw, the progress that the scientific community has made in controlling the assembly of substances on the atomic-layer scale has opened our eyes to a whole new world of artificially structured materials that have fundamentally different properties than have been seen in the past. Before we introduce what is known about the physics behind this new behavior, we begin with a discussion of the GMR effect, whose discovery lit the fuse that led to the explosion of activity in this new field.

1.2.1 Spintronics -- one of the most significant developments of the 1990's.

Electrons have an inherent property called charge, and it is this property that allows us to force them to flow as current through the circuits in the appliances and computers around us. Electrons also have an inherent quantum mechanical property called **spin**. The current in an electronic device is composed of current due to moving *spin-up* electrons and moving *spin-down* electrons. Until recently, electronic devices did not use this additional information carried by the current. Innovative scientific investigation was required to learn how to take advantage of this additional electronic property.

In 1988, **giant magneto-resistance (GMR)**, an effect that allows us to exploit electron spin in devices, was discovered in layered metallic structures [5]. The simplest such device, a **spin-valve**, is shown in Fig. 1.3. It can be thought of as a sandwich – a thin film of non-magnetic material between two thin films of magnetic

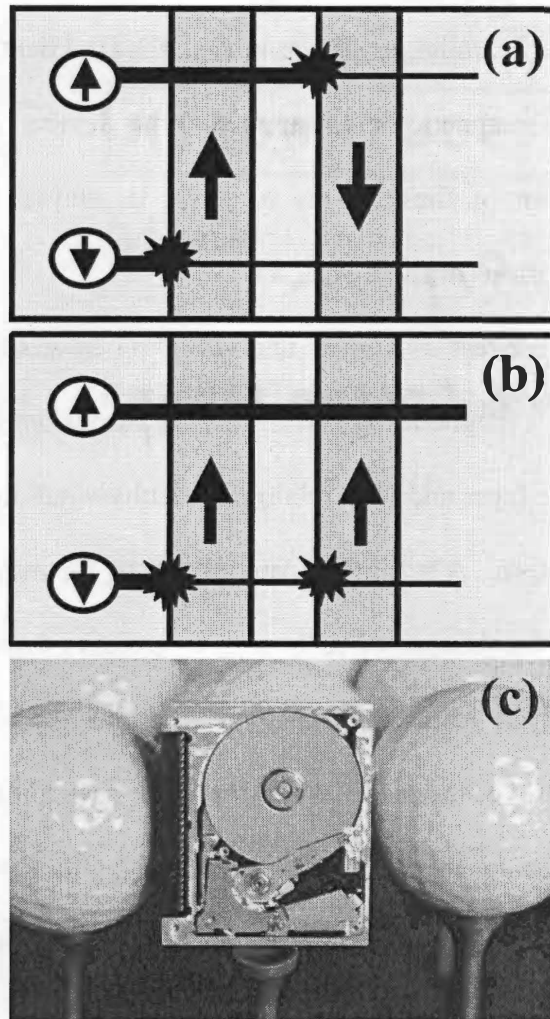


Figure 1.3: Spin-valves -- the simplest spintronic devices. (a) When no magnetic field is applied to a spin-valve, the magnetic moments of the two magnetic layers (dark regions) are anti-parallel. In this case, spin-up and spin-down electrons have an equally difficult journey through the device. (b) When a field is applied to the device, the magnetic layers can become magnetized in the same direction. This allows electrons of one spin travel through the device with relative ease, resulting in a decrease in the total resistance. This is the GMR effect. (c) The Travelstar™ disc that is produced by IBM uses a spin-valve head to read data that is recorded at a density of 4.1 billion bits per square inch. More recent devices achieve bit densities approaching 20 billion/in².

material. The magnetic layers can be magnetized along a particular direction, as shown by the light and dark arrows in the figure. Initially, the magnetization of these layers is opposite, or anti-parallel, as shown in Fig. 1.3(a). Giant magneto-resistance is seen when an external magnetic field is applied to this device. As the external field forces the magnetization of these layers to align, as shown in Fig. 1.3(b), the resistance of the device drops drastically.

The following concept is key to understanding how spin valves work: an electron moves through a magnetic layer with relative ease when its spin is parallel to the magnetization of the layer and with relative difficulty when its spin is opposite to the magnetization direction. A magnetic material that is, for instance, magnetized in the “up” direction can be thought of as having an excess of spin-up electrons and empty spin-down electron levels. Spin-down electrons tend to scatter into the available spin-down states of the material and therefore have a more difficult journey through it than the spin-up electrons. When no magnetic field is applied to the device, as in Fig. 1.3(a), the magnetic layers are anti-aligned and both spin-up and spin-

down electrons are scattered equally. When a field is applied, as in Fig. 1.3(b), it is like opening a valve – spin-up electrons are allowed through, resulting in a large decrease in the resistance.

GMR devices like the one shown in Fig. 1.3 are excellent magnetic field sensors. For this reason, they are already in widespread use as read heads for computer disk drives. In read heads, one of the magnetic layers has a magnetization that is pinned in one particular direction. The magnetization of the other layer can be

flipped by the magnetic field caused by magnetic “bits” written on the hard drive that spins underneath it. Passing a test current through the device immediately identifies whether the layers of the read head are aligned parallel or anti-parallel, therefore reading the bit written on the disk. These devices can be manufactured on very tiny (≈ 10 nm) length scales and are sensitive enough to read magnetic bits of similar sizes. An example of the technological impact of the discovery of GMR is the IBM Travelstar™ disk shown in Fig. 1.3(c) that operates with a bit density of 4.1 billion bits per square inch. More recently, this technology has allowed bit densities of 56 Gbits/in² to demonstrated in the laboratory and has the potential to increase to 300 Gbits/in² [6]. The development of spin electronics is clearly one of the greatest technological achievements of the 1990’s. This field evolved from scientific discovery to development to production in less than a decade and has benefited every one of us who uses a computer.

The important point here is that the new physics, surprises, and benefits associated with spintronics were discovered because of pioneering work on *reduced-dimensional* systems. GMR devices are two-dimensional in the sense that their length scale is small enough along one particular direction to awaken quantum mechanical effects that are not seen in larger structures. Nanometer layer thicknesses are absolutely essential for the effects of spin to play a role in the conduction properties of these devices. In the section that follows, we will discuss why this is the case, and why we can look forward to uncovering more exciting new physics in ultrathin film, nanowire, and quantum dot systems.

1.2.2 Why should we expect exotic new effects in magnetic nanostructures?

Length scale effects

One source of unexpected behavior in nanoscale systems is what may be referred to as "characteristic length effects". We might guess that new phenomena emerge when a system is reduced to a size that is comparable to the characteristic length over which some physical process occurs. This is seen in spin-valves in that the spacing between magnetic layers must be shorter than the so-called "**spin diffusion length**" for electrons in the device. The spin diffusion length is the average distance that an electron can travel before its spin is flipped (from up to down, or vice versa) due to collisions with other entities in the material. This distance, for example, can be as large as several μm in "noble metals" like Cu, and as small as 10-50 nanometers in metals with spin impurities as scatterers [7]. If the magnetic layers were too far apart in these structures, GMR would not be seen because the electrons that carry the current would essentially "forget" their spin before reaching the next magnetic layer. Half of the electrons would have the "wrong" spin relative to the magnetic layer, whether the magnetization of the layer was up or down. Again, nanometer layer thicknesses are absolutely essential for these devices to function.

Other important characteristic lengths in magnetic systems include the domain size and the domain wall width. In thin (4 - 60 atomic layer) films of iron [8] and nickel [9] on Cu(100), domains are 10-100 μm and 5-20 μm across, respectively. Domain wall widths can range from tens of nanometers to values as small as single

atomic spacings. In Chapter 5, we will discuss work that is being done to establish the interplay between magnetic domains and field-dependent transport.

Interface, neighbor-atom, and dimensionality effects

Generally speaking, we might expect new behavior in nanostructured systems due to the fact that interfacial and boundary effects become relatively more important as the size of the object is decreased. In a macroscopic chunk of iron, the ratio of the number of surface atoms to bulk atoms is $10^{15}:10^{23}$, or 0.00000001. In a cube of bcc Fe measuring 5 nm on an edge, this ratio is 2000:12000, or 16.7%.

The tendency for this increase in the ratio of surface to bulk atoms to, for instance, influence the average atomic moment of a system can be illustrated by comparing the magnetic moment of a single iron atom to that of an iron atom embedded in a bulk chunk of Fe. The six $3d$ electrons of an iron atom populate specific atomic energy levels such that the moment of a single atom is predicted to be $6.7 \mu_B$, as shown in Fig. 1.4. Electrons in a large cluster of Fe atoms are itinerant, or not confined to individual atoms, and "live" in energy bands. This modifies the electronic structure such that the measured value of the average moment per atom is decreased to $2.2 \mu_B$ in bulk Fe. From this, we can see that as we nanostructure Fe and reduce the number of nearest neighbors that the average atom has, we may expect to see the moment per atom increase from $2.2 \mu_B$ toward the atomic value. This increase in the average atomic moment has been found, for example in Fe films on tungsten [10] and in studies of Fe clusters [11].

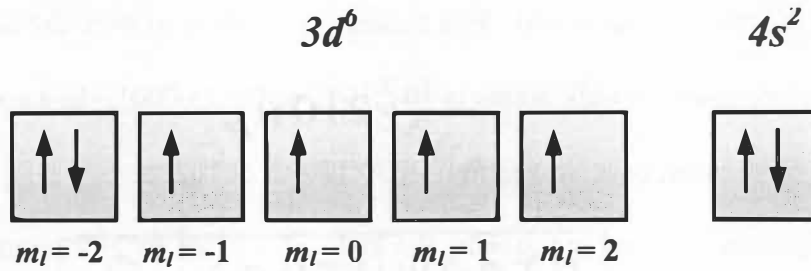


Figure 1.4: Electronic levels and magnetism in a single iron atom. An iron atom has the core electron structure of argon and a $3d^6 4s^2$ valence configuration. The spin contribution to the magnetic moment is $4\mu_B$, as seen by the four unpaired electrons. Since the atom has quantum numbers $s = 2$, $l = 2$, and $j = 4$, the total moment (from spin and angular momentum) is found to be

$$\mu_{Fe} = g_j \sqrt{j(j+1)} \mu_B = \left(1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2(j+1)} \right) \sqrt{j(j+1)} \mu_B = 6.7 \mu_B,$$

Where g_j is the Lande g factor for the atom. The atomic moment is considerably higher than the per atom moment in bulk Fe ($2.2\mu_B$).

In addition, simple magnetic models predict that the temperature at which a magnetic system orders should decrease as it is nanostructured due to pure "dimensionality" effects. One simple model is the Ising model, in which atomic moments ($\vec{S}_i$) are forced to point in either an "up" or "down" direction and interact with each other with some strength usually denoted by the symbol J . The interaction energy is often called "exchange energy" and is usually written in the following way;

$$E_{ex} = \sum_{ij} -J \vec{S}_i \cdot \vec{S}_j$$

Moments confined to a three-dimensional cubic lattice are found to order below a temperature of $T_c = 4.5 J / k_B$ [12]. The Curie temperature for the corresponding 2-D system, in which individual atoms only have neighbors on a square lattice within a plane, is found to be lowered to $2.269 J / k_B$ [12]. In one dimension, the Ising system isn't predicted to order at all.

Energy levels and quantum effects

The most important possible sources of exotic new behavior in nanoscale systems are quantum mechanical effects. Quantum mechanics tells us that electrons in solids have inherent wavelengths that are related to their momenta. Since quantum effects appear when materials are confined to length scales on the order of these wavelengths, they could easily have been included in the sub-section that addressed characteristic length effects in nanostructures. We treat these effects separately here,

however, because they show that both length scales and *energy scales* have to be considered in tailoring nanostructured systems.

As undergraduates, we all learned that shrinking an object causes its seemingly continuous distribution of electronic energy levels to become more discrete. This effect is shown for the simplest possible case (a free electron gas) in Fig. 1.5. In a macroscopic, 3-dimensional collection of free electrons, the density of available states ($D(E)$) grows as the square root of the energy (E) of the states. In a one-dimensional system (i.e. one that is confined in two directions) the density of states becomes a train of singularities that diverge as $1/E^{1/2}$. In an extreme case in which a collection of electrons is confined in all three directions, the distribution of energy levels becomes a series of delta functions that occur at energies given by the particle-in-a-box model. Namely, these levels are given by

$$E_{n_x, n_y, n_z} = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8ml^2}$$

in which n_x , n_y , and n_z are integers greater than zero, h is Planck's constant, and m is the electron mass.

The important thing to note here is that in nanostructured materials, the positions of these levels can be tuned by adjusting the size (l) of the region of confinement. As shown in Fig. 1.5, this makes it possible to tune the density of states at the Fermi energy (E_f), which is the location of the boundary between the highest occupied and lowest unoccupied levels. The distribution of electronic states near the Fermi energy plays a role in all aspects of how solids behave; it not only determines

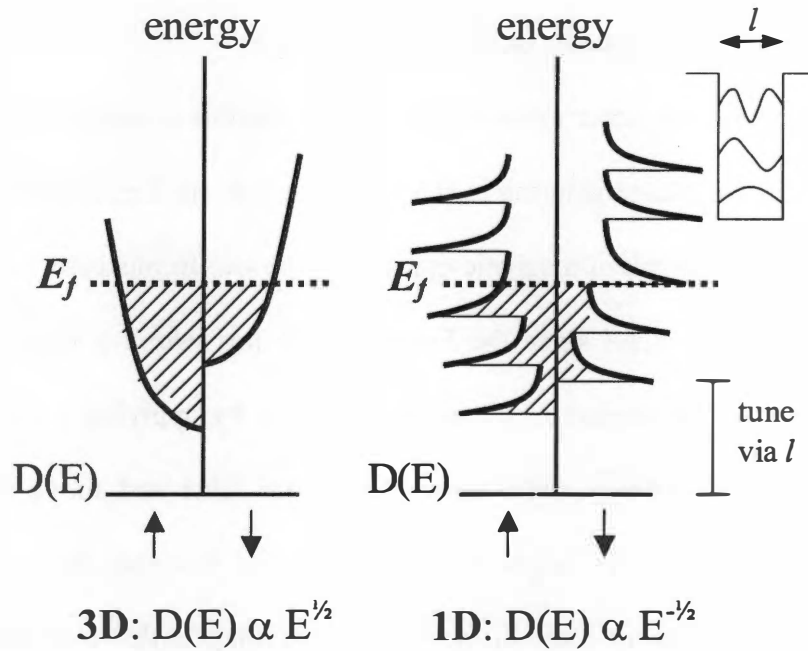


Figure 1.5: The effect of confinement on the density of states of free electrons [adapted from ref. 7]. In a three dimensional free electron gas, the density of states grows like the square root of the electron energy. In a one-dimensional system, the density of states is a train of $1/E^{1/2}$ singularities. The positions of these singularities are sensitive to the size (l) of the well in which the electrons are confined. The key point here is that in confined systems, the positions of the peaks in the density of states can be adjusted relative to the Fermi level (E_f) [7]. This can have profound effects on the behavior of the systems, as described in the text and in Figure 1.6.

whether or not solids are magnetic or conducting, but can also drive exotic transitions like superconductivity or lead to the formation of charge density waves [7]. Placing a large peak in the density of states at E_f creates a highly unstable situation. The energy of the system can be changed drastically (and perhaps minimized) if the system undergoes a structural, magnetic, or electronic transition.

An exciting, but rather extreme view of the possible consequences of shifting electronic states via nanostructuring is shown in Fig. 1.6. In Fig. 1.6(a), a simplistic band structure for a chunk of magnetic material is shown. In this case, we know that we have a magnetic *metal* since the Fermi energy lies *within* a band of allowed energy levels. (If we attempt to excite the electrons by applying a bias, they can easily find available energy states above the Fermi level and move through the material as current.) If we begin nanostructuring the material, the energy bands narrow, or begin to become more discrete. One can imagine that they might narrow such that the Fermi energy falls *within* a spin-up energy band and *between* spin-down energy bands. This scenario is shown in Fig. 1.6(b). In this case, we would have a truly exotic magnetic material; its spin-up electrons would flow freely as if it were a metal, but its spin-down electrons would be rendered immobile by the energy gap between occupied and unoccupied states.

Searching for these "half-metals" has become an active area in condensed-matter physics. Half-metals would lead to drastic improvements in the performance of GMR spin-valves. Conventional spin-valves can be adjusted between high-current (parallel moment) and low-current (anti-parallel moment) states. Spin-valves

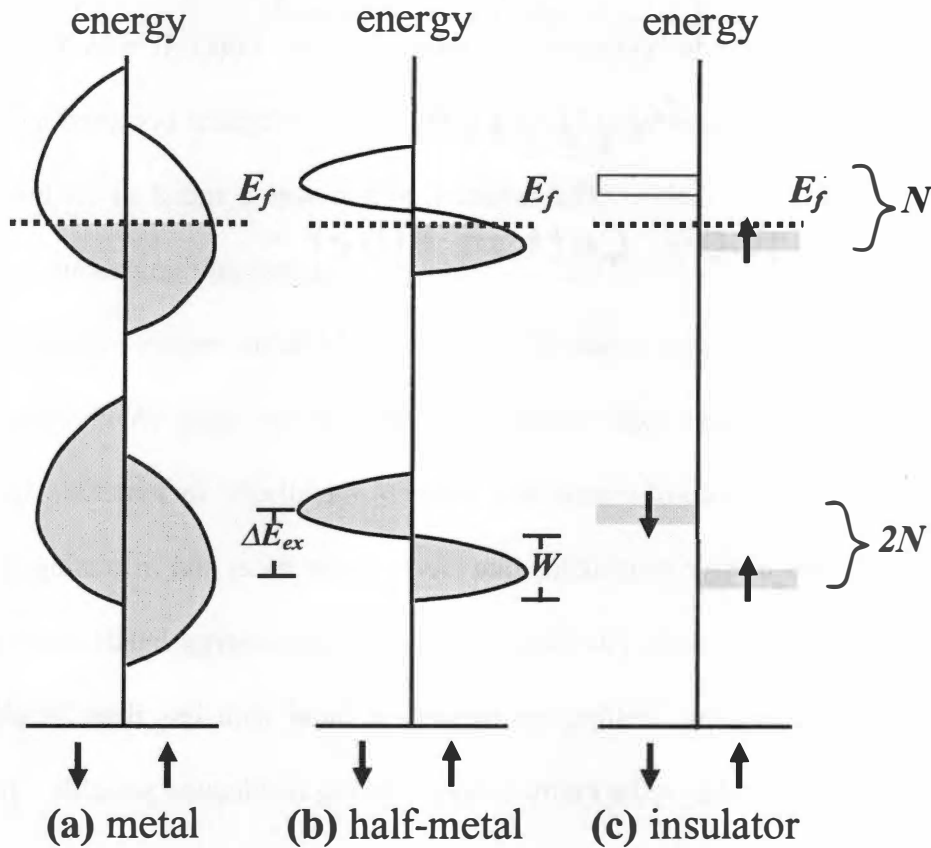


Figure 1.6: Tuning electronic states via nanostructuring. This simple schematic illustrates what might happen to the spin-up and spin-down electron energy states of a magnetic metal as it is nanostructured. Shrinking an object narrows its electronic energy bands. With this in mind, one can envision that nanostructuring could cause the distribution of levels for a particular material to shift about its Fermi energy (E_f) such that the material is transformed from (a) a bulk metal to (b) a "half-metal" in which transport only occurs in one spin channel to (c) an cluster of N atoms that would be an insulator. This interesting behavior would appear as the spread in energy of a particular sub-band (W) became less than the splitting of the spin-up and spin-down sub-bands (ΔE_{ex}).

fabricated with half-metals could be adjusted between high-current and *zero*-current states. They'd be *perfect* switches!

Upon shrinking the material further, the energy levels would continue becoming more and more discrete. As shown in Fig. 1.6(c), it would eventually become the case that there would be a gap between the highest occupied and lowest unoccupied electronic levels. The material, which was a metal in its bulk form, would therefore be transformed into an insulator. The unusual thing about the energy level diagram in Fig. 1.6(c) is that the material would be an insulator despite the fact that its highest occupied band contains one electron per atom (N electrons for N atoms). There is a rule-of-thumb that predicts metallicity in materials when the highest populated energy band holds one electron per atom and insulating behavior when it holds two electrons per atom. This is because energy bands can typically accommodate $2N$ electrons. Filling the uppermost band with less than $2N$ electrons would leave empty states at the Fermi energy, making conduction possible. The case depicted in the figure, however, is exceptional because the splitting between the spin-up and spin-down sub-bands (ΔE_{ex}) is so much larger than the energy spread of the sub-bands (W), that the spin-up and spin-down sub-bands do not overlap. In this case, the spin-up and spin-down sub-bands have become two truly separate bands that can each accommodate only N electrons. This makes the rule of thumb invalid; the electrons can't move despite the fact that there are only N of them in the uppermost band.

Nothing as drastic as the chain of events depicted in Fig. 1.6(a), 1.6(b), and 1.6(c) has yet been observed. This example, however, highlights the role that the

energy bandwidth (W) and exchange splitting (ΔE_{ex}) could have in nanostructuring magnetic systems. The scenarios shown in Fig. 1.6(b) and 1.6(c) could arise from two factors; a reduction in W or an increase in ΔE_{ex} . The magnitude of ΔE_{ex} is proportional to the strength of the interaction between neighboring moments (usually denoted by the symbol J) and the size of the moments. There is no particular reason to expect the strength of the *interaction* between moments to change as an object is nanostructured, but we have already seen that the magnetic moments themselves *do* change. They tend to increase and approach the value of the atomic moment as an object is nanostructured. This effect, and the corresponding effect on the exchange splitting (ΔE_{ex}) has been observed in one- and two-monolayer films of Fe on the tungsten surface [10].

While the dream depicted in Fig. 1.6 has not yet been realized, the quantum nature of confined electrons has been found to lead to exotic behavior in nanostructured materials. One stunning example is found in the interaction between magnetic layers in spin-valve sandwich structures. For spin-valves to function, the magnetization of the magnetic layers must spontaneously align anti-parallel in the absence of a magnetic field. As it turns out, spaced magnetic layers interact with each other and can align parallel, anti-parallel, or not at all, depending on the spacing between them [13-14]. This behavior is shown in Fig. 1.7 for the case of an iron film that is separated from an iron substrate by a chromium spacer layer. The experimentalists grew the spacer layer in the form of a wedge (see Fig. 1.7(a)) in order to make it convenient to study how the relative alignment of the magnetization of the iron layers varies with the spacer thickness. The surprising behavior of this

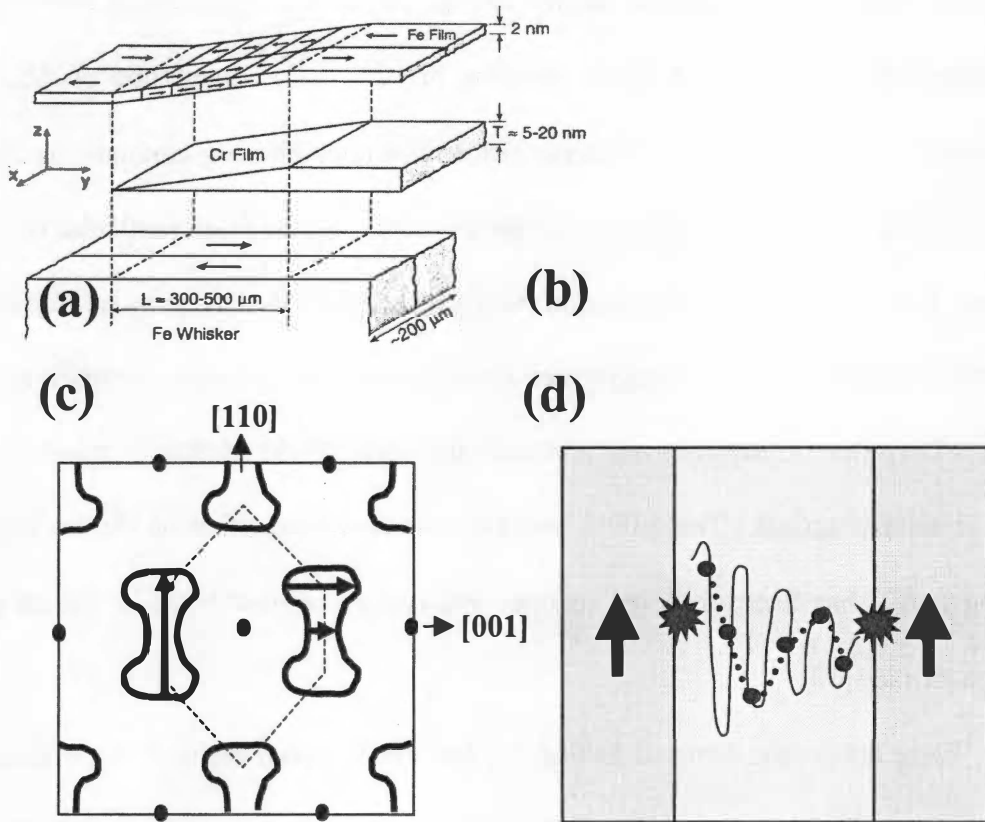


Figure 1.7: Oscillatory exchange coupling in magnetic multilayer structures [(a) and (b) from ref. 13]. (a) Schematic of a multilayered structure made up of an iron sample and iron film separated by a non-magnetic chromium wedge. (b) Image of the magnetic domain structure of a smooth (top) and rough (bottom) iron overlayer. The white areas indicate where the magnetization points to the right and the black areas show where it points to the left. The chromium spacer layer thickness varies linearly along the length of the sample and is plotted on the horizontal scale. This allows the dependence of the coupling between the magnetic layers to be studied as a function of the spacing between them. Two periodicities (0.2 nm and 0.8 nm) can be seen in the smooth film. The rough film (bottom) disturbs the reflection of electron waves such that the short periodicity is not observed in that case. (c) Multiple "nesting" vectors in the Fermi surface of copper, which lead to multiple periodicities in interlayer coupling in Fe/Cu/Fe sandwich structures. (d) The coupling between the magnetic layers oscillates in sign and decays with distance, as shown in the solid curve at the bottom of the figure. Since it is only possible to sample this interaction at particular locations (black dots) that are integer multiples of the lattice constant of the spacer layer away from the substrate interface, longer periods in the oscillation of the magnetic coupling are often observed. This longer periodicity is indicated by the dotted curve.

system is shown in Fig. 1.7(b). As the thickness of the spacer is increased, the relative alignment of the magnetization of the iron layers switches back and forth periodically from being ferromagnetic to being anti-ferromagnetic.

This behavior is related intimately to quantum well states in the spacer layer. Studies of magnetization oscillations in this and other systems have led to the finding that the periodicity corresponds to the Fermi wavelength of electrons in the spacer layer. The sign of the spin-polarization that the spacer electrons communicate to the electrons in the film depends on the fraction of whole oscillations that the spacer electron wavefunctions complete in the region between the magnetic layers.

In many cases, as in the Fe/Cr system above, more than one periodicity has been observed in the interlayer coupling. One origin of multiple periodicities is the fact that real metals have more than one Fermi wavelength due to the non-spherical (non-free-electron-like) shape of their Fermi surfaces. Interlayer coupling periods have often been found to occur with wavelengths ($\lambda_j^* = 2\pi/k_j^*$) given by particular set of wavevectors (k_j^*) that span the Fermi surface along the direction perpendicular to the layer plane. These particular wavevectors are said to be "nested" and are shown in the Fig. 1.7(c). It is also the case that periodicities in the interlayer coupling that are much longer than the Fermi wavelength of the spacer layer electrons have been observed [14]. These mysterious longer-range oscillations have been found to match the specific length over which the Fermi wavelength of the electron and the grid of the atomic lattice of the spacer layer form "beats". This effect has been called "aliasing" and is shown in the lower right in Fig. 1.7(d).

In the preceding discussion about spin-valves, we learned that useful, new effects appeared in two-dimensional multilayer structures when one length scale in a magnetic system was reduced to a regime governed by quantum effects. This is perhaps hinting that there are more surprises in store in one-dimensional (quantum wire) and zero-dimensional (quantum dot) systems. We then saw that nanostructuring can new electronic states and surface phenomena, and that it can cause significant changes in the transport properties, magnetic moment, and ordering temperature of a substance. In short, we have seen that through artificial fabrication on the nanoscale, one can create entirely *new* behavior.

1.3 What are the major challenges in this field?

Progress in three interrelated areas has generated the discoveries and excitement that have marked the exploration of magnetic nanostructures over the last 15 years. Indeed, advances in characterization, synthesis, and realistic modeling of the behavior of various forms of nanostructures have fueled the increasing activity in this field. As we will see, each of these areas is intimately related to the others and all of them present challenges that we must meet in order to understand the processes that determine the behavior of artificially structured materials. In this section, we discuss these challenges, along with others that exist in the field. Once these challenges are met, we will ultimately have the concepts and tools needed to *design* these materials, or tailor them to do what we want them to.

1.3.1 Challenges in characterizing nanoscale objects

Characterization of magnetic nanostructures once was a tall hurdle to clear. How can a scientist trying to grow nanopatterned objects be sure that she has done so? How can we observe the tiny magnetic response of an object that consists of, at most, a few layers of atoms? In order to understand the physics of these systems, it has been necessary to attempt to tackle these difficult tasks. From this, we can see why progress in our understanding of magnetic nanostructures has been intimately tied to the development of characterization techniques.

For studying the growth and morphology of nanostructures, perhaps no technique has been as important as scanning tunneling microscopy [15]. The scanning tunneling microscope (STM) is routinely capable of 0.1-0.01 Å resolution in the vertical direction and can easily image structures whose lateral dimensions are on the nanometer scale. Under the right conditions, atomic resolution can be achieved. (Examples of high-resolution STM images can be seen by skipping ahead in this chapter to Figs. 1.11 and 1.13.)

Although quite a bit of skill is required to build an STM that functions well, the principle behind its operation is rather simple. A small voltage, typically ~ 1 V, is placed between a sharp metallic needle, or “tip”, and a sample. The current that is made to flow between this tip and the sample is extremely sensitive to the separation between them. This is due to the fact that the likelihood of an electron to jump, or tunnel, across a gap from one metal to another is exponentially dependent on the distance between their separation. The tip is precisely scanned over the surface by

piezo-electrics, which are materials that change their length when voltages are applied to them. As it scans, the instrument can be operated in a “constant height mode”, such that the tip is forced to stay at a constant vertical position over the sample and changes in the tunneling current are recorded. Alternatively, it can be operated in “constant current mode”, in which the z-piezo voltage is constantly changed and recorded as it changes the vertical position of the tip in order to maintain a constant flow of electrons between the tip and sample. These modes of operation are shown in Fig. 1.8(b). In either case, the resulting maps of current or voltage vs. tip position are closely related to topography, although they also contain information about local changes in the electron density and work function of the sample.

Since the operation of the STM depends on a current between the probe and the sample, the technique is limited to the study of metallic or semiconducting systems. The STM will be used extensively to study the metal-on-metal systems that we will discuss in Chapters 3 and 4. If one attempted to use an STM to image an insulating system, like isolated Fe particles on NaCl, the tip would continuously approach the sample as it struggled in vain to establish tunneling current, and would eventually crash into the surface. For insulating systems, the instrument of choice is the atomic force microscope, or AFM [16]. In an AFM, the forces (van der Waals and others) between the atoms of a sample and probe tip are monitored instead of tunneling current. The tiny mechanical response of the tip to these forces is usually monitored with an “optical lever” technique (as in Fig. 8(a)) in which the deflection of a laser beam that is reflected off of the back of the tip is measured. Representative

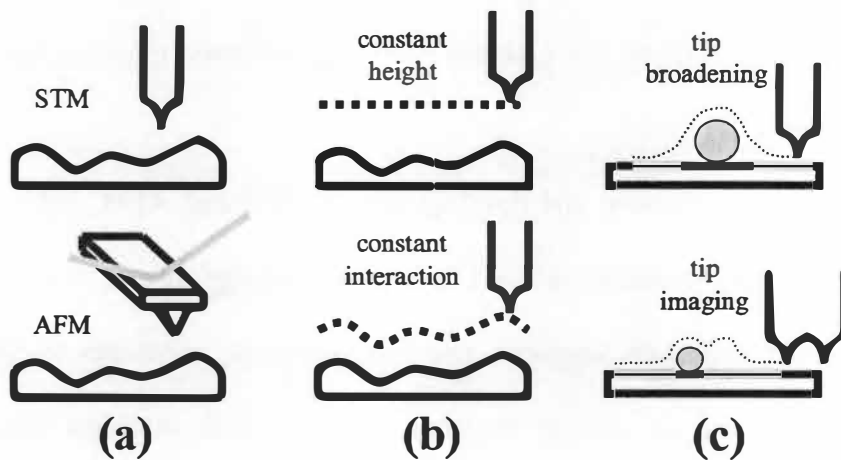


Figure 1.8: Scanning tunneling and atomic force microscopy. (a) In STM, a bias is placed between a sharp tip and a sample. The likelihood for electrons to tunnel between the tip and sample depends exponentially on the separation between the tip and sample. In AFM, the motion of a cantilever tip is monitored by bouncing a laser beam (grey line) off of the back side of the cantilever. Changes in the frequency of vibration of the cantilever depend on the local force gradient above the sample. (b) Probe microscopes like STMs and AFMs can be operated in "constant height" mode, in which changes in the tip-sample interaction are monitored as the tip is scanned, or in "constant interaction" mode, in which changes in the vertical position of the tip are monitored. (c) Difficulties inherent to nanoscale imaging in both techniques include broadening of features due to the shape of the tip and the appearance of extra features in images when the object being imaged is smaller than features on the probe tip.

AFM images can be found in Chapter 5, in which we treat magnetic films, wires, and dots grown on an insulating substrate.

Both of these probe microscopies are severely limited in their ability to image nanostructures with high height to width ratios, such as quantum dots. Probe tips cannot be perfectly sharp, and this results in significant broadening and distortions. These effects are shown schematically in Fig. 1.8(c). These problems are always present, to varying degrees, and care has to be taken to avoid misinterpreting images because of them.

Due to the invention and development of STM and AFM, determining the morphology of nanostructures is much less of a challenge than it was two decades ago. Characterizing their magnetic response, however, continues to be a major obstacle. Measuring the *overall* magnetic response of an ultrathin film, array of nanowires, or collection of quantum dots that is made from less than a single atomic layer of material may sound daunting, but is actually achievable with an increasingly popular technique called the surface magneto-optical Kerr effect (SMOKE) [17]. The physical principles behind this approach and the practical details of how it is practiced are treated in Chapter 2. Observing magnetic domain structure, or the magnetic response of *individual* nanostructures is an even greater challenge. Whether or not a magnetic system is nanostructured, the competition between exchange, anisotropy, and dipolar interactions that determines domain structure often results in domains that are on the order of 10 to 100 nm. Observing these domains remains one of the most important technical difficulties in the field, and has led to the development of several cutting-edge techniques. The most popular approaches are

summarized in Table 1.1. In the following, we will take closer looks at the most widely used method, scanning electron microscopy with polarization analysis (SEMPA) and at spin-polarized scanning tunneling spectroscopy (SP-STs), which is the method that seems most likely to give us an understanding at the smallest length scale.

The principle of operation for SEMPA [18] is shown in Fig. 1.9. A beam of ~ 5 keV electrons is focused to a tiny (< 100 nm) spot on the surface of a ferromagnet. The incident electrons excite secondary electrons that originate from that point on the surface. The polarization (excess of one spin over the other) of these secondary electrons can be measured. It has been observed that the secondary electrons tend to have their magnetic moments parallel (and thus spins anti-parallel) to the magnetization of the sample at that spot. Because of this, a map of the sample magnetization can be generated by rastering the focused beam point-by-point across the surface and measuring the electron polarization at each step. Resolution on the order of 20 nm can be achieved and advantages of the technique include a tremendous depth of field, the fact that it can be used at both high and low magnification, and that it can image two components of the magnetization simultaneously. The fact that the technique uses electrons means that it has difficulty imaging buried layers, and doesn't work well in the presence of applied fields due to the Lorentz force on the electrons.

A particularly exciting new technique is a spin-polarized version of scanning tunneling microscopy that was developed by Bode, Getzlars, and Wiesendanger in 1998 [26]. The technique exploits the difference in the probability for up or down

Table 1.1: Popular magnetic domain imaging techniques. SEMPA stands for Scanning Electron Microscopy with Polarization Analysis, LEEM signifies Low Energy Electron Microscopy, and SQUID stands for Superconducting Quantum Interference Device. The resolution values shown reflect the lateral resolution that one can obtain when the techniques are pushed nearly to their limits [18-26]. One group is currently expanding the capabilities of SEMPA such that it is becoming possible to image in the presence of a modest external magnetic field [23].

Technique	Principle	Resolution	Advantages/Disadvantages
SEMPA	Incident electron beam creates secondary electrons whose polarization reveals local magnetization.	20 nm	Can get separate components of magnetization. Large depth of field. Can't image buried layers or in an applied field. Requires ultra-high vacuum.
LEEM	Reflectivity of incident polarized electron beam depends on orientation of sample magnetization relative to polarization.	20 nm	Can get separate components of magnetization. Large depth of field. Can't image buried layers or in an applied field. Requires ultra-high vacuum (UHV).
Kerr microscopy	Polarized incident light undergoes polarization & ellipticity change that is proportional to magnetization	200 nm	Can get separate components of magnetization. Can image in applied fields. Resolution limited by wavelength of light.
MFM	Magnetic force gradient causes change in vibration frequency of cantilever probe tip.	100 nm	Can image samples with protective coatings. Can image in applied fields. Can image insulators. Sensitive to stray fields, but not magnetization. Images are difficult to interpret. They depend greatly on the tip condition, which isn't known.
Spin-polarized STM	Different tunneling probability for spin-up and spin-down electrons between sample and magnetic probe tip.	0.1 nm	Very high resolution. Can image in applied fields. Works only on metal-on-metal or metal-on-semiconductor systems. Only proven on a few systems so far. Requires UHV.
Scanning SQUID	Small magnetic flux detection coil is scanned over surface.	4000 nm	Most sensitive method for quantitative measurement of stray fields. Sensitive to stray fields, but not magnetization. Severely limited spatial resolution.
Bitter	Tiny particles are dusted on a sample, allowed to align with stray field lines, and then imaged.	100 nm	Relatively simple technique. Requires that sample be coated with particles, often from solution. Not quantitative. Measures stray fields only.
Lorentz Microscopy	High energy electron beam is focused to a sharp spot and is shot through a sample. The Lorentz force deflection of the beam due to the local B field is easy to calculate.	10 nm	Very high resolution. Sample has to be shaved or etched so that it is very thin. This can modify its domain structure.

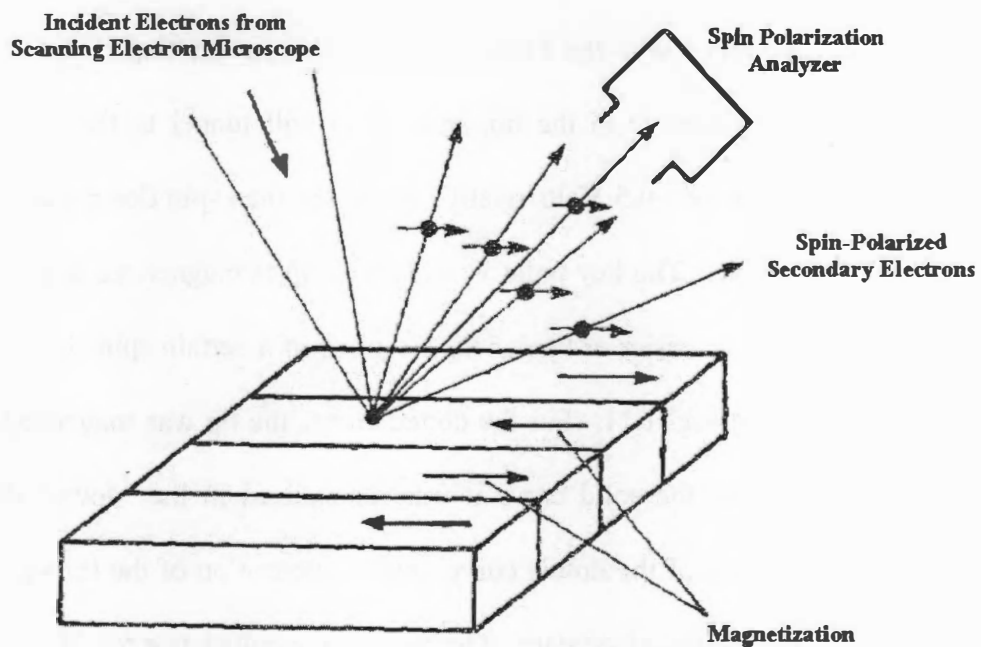


Figure 1.9: The principle of operation for SEMPA [from ref. 14]. An incident beam of unpolarized electrons is focused to a spot on a sample. The polarization of the outgoing, secondary electrons yields information about the magnetization of the sample, as described in the text. An image of domain structure recorded with the technique can be seen in Fig. 1.7(b).

electrons to tunnel from a sample to a tip that is magnetized in a particular direction. The remarkable resolution of this technique is seen in Fig. 1.10. The difference in tunneling was first demonstrated by imaging a Gd(0001) surface with an Fe coated W tip. The Gd surface was ideal for this experiment because it was previously known that that material has a surface electronic state such that there were occupied majority (spin up) levels 0.2 volts below the Fermi energy and unoccupied minority (spin down) levels 0.5 volts above the Fermi energy. This means that if the sample is biased at -0.2 volts relative to the tip, spin up e^- will tunnel to the tip from the sample. If it is biased at $+0.5$ Volts relative to the tip, then spin down electrons will tunnel into the sample. The key point is that if the tip is magnetized in a particular direction, then it will be easier or harder for electrons of a certain spin sign to tunnel. This effect is seen in Fig. 1.11. For the dotted curve, the tip was magnetized in the “up” direction and for the solid curve it was magnetized in the “down” direction. Apparently, in the case of the dotted curve, the magnetization of the tip was aligned with that of the majority surface state. The tunneling conductance out of that state is higher for the dotted curve. With this information, one would then predict that the conductance into the minority state should be lower with the tip magnetized in this direction. By looking at the difference in conductivity when the bias is $+0.5$ V, we see that this is indeed the case. It is possible to plot domain contrast by recording these spectra at each pixel, and plotting the asymmetry in the conductivity σ , which is given by $(\sigma_{\text{majority}} - \sigma_{\text{minority}}) / (\sigma_{\text{majority}} + \sigma_{\text{minority}})$ vs. the tip position.

This technique is in its infancy, but is already very promising. In one case, SP-STs has been used to observe anti-ferromagnetic ordering with atomic resolution

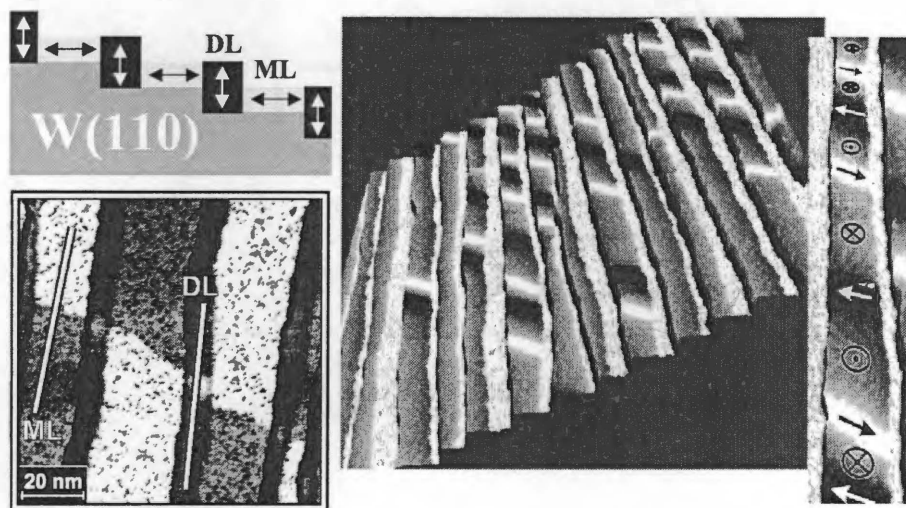


Figure 1.10: Magnetic domain structure of Fe nanowires as measured with spin-polarized STM [from refs. 24 and 25]. Depositing between 1 and 2 atomic layers of Fe on a specially prepared W(110) surface results in alternating monolayer (ML) and double layer (DL) nanostripes, as shown in the schematic in the upper left. The arrows indicate the directions in which the easy axes of the ML and DL stripes are typically found. By taking scans across domain walls (along the lines scans shown in the image at the lower left) domain wall widths were found to be 0.6 ± 0.2 nm and 3.8 ± 0.2 nm for single and double layer ribbons, respectively. The image at the right shows a spiral spin structure (narrow inset at far right) found in the double layer stripes when 1.6 atomic layers of Fe were deposited on the sample.

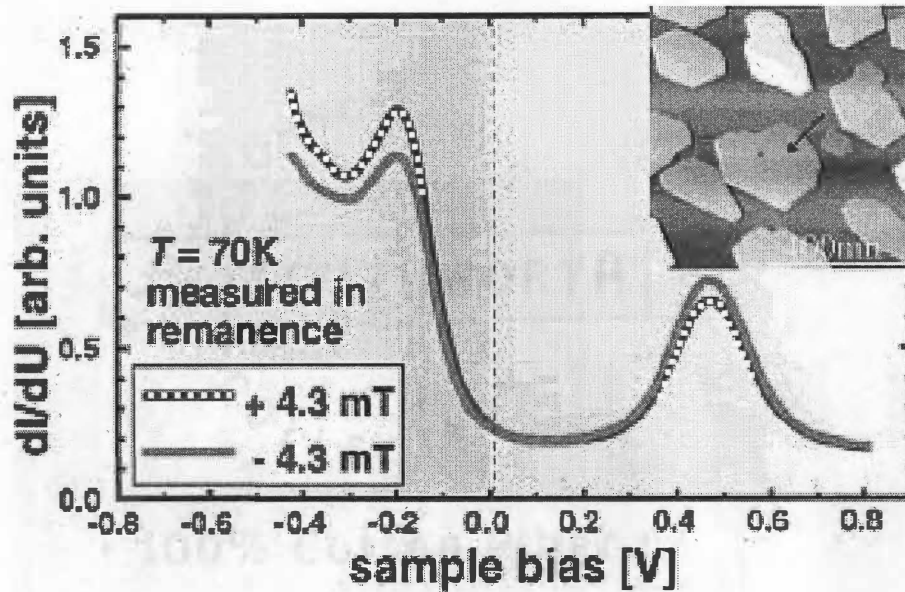


Figure 1.11: Spin-dependent tunneling -- the principle behind spin-polarized STM [from ref. 26] This figure is a plot of the conductance of electrons between an iron-coated tungsten STM tip and gadolinium sample as a function of the bias between the tip and sample. The tip was held still over the spot indicated by the arrow in the inset image at the upper right. A field was then applied to the Gd sample in order to saturate its magnetization in a particular direction in the plane of the surface. Then, the field was reduced to zero and the curves were recorded. The dotted curve was recorded with the sample magnetized in the same direction as the iron-coated tip and the solid curve was taken with the sample magnetized in the opposite direction. The differences in conductivity that are observed at certain bias voltages are explained in the text. The fact that the conductance depends on the magnetic state of the sample means that it can be used to distinguish magnetic domains, as shown in the previous figure.

[27]. STS made it possible to study domain formation in Fe nanowires on W(110) [24-25]. This shows clearly how scientific progress in this field is being driven by the development of an experimental technique.

1.3.2 Difficulties in synthesis and overcoming template effects

Synthesis of magnetic nanostructures also continues to be a challenge. How does one get magnetic atoms to line up, group, and/or form patterns in certain, useful ways? One approach is to use “brute force”, and burn or draw each nanoparticle individually. This is called lithography. Three very commonly used tools for this type of nano-fabrication are photolithography, electron beam lithography, and ion beam milling. In photolithography, a chemical called photo resist is spread on a surface. A desired pattern is made in the photo resist with light, using with an interference pattern or a mask. In the case of photolithography, the minimum size of features in the pattern is limited by the wavelength of light. The most advanced practitioners can produce 150 nm objects with this approach. Burning or drawing patterns with electron or ion beams can produce features in the 70-100 nm size range.

Lithography can be achieved on the atomic scale with skillful use of an STM tip, as shown in Fig. 1.12. In figure 1.12(a), atoms were removed by high current in the vicinity of the tip as it traced out the lettering. In 1.12(b), individual Fe atoms were pushed into the “quantum corral” that is shown. This approach is extremely precise, but also extremely slow and difficult.

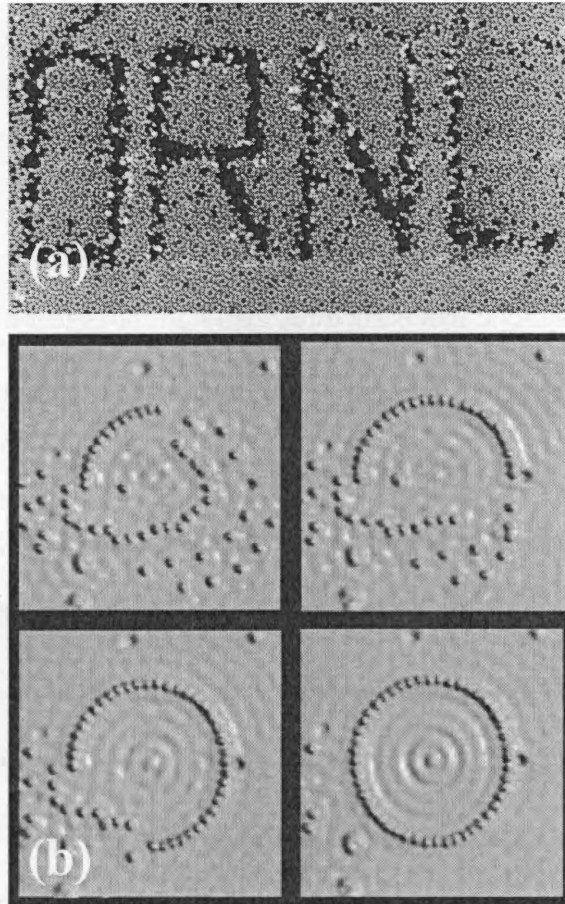


Figure 1.12: Examples of nanoscale and atomic precision in lithography with an STM. (a) Using a very high tunneling current made it possible to scrape this pattern on a silicon surface [28]. (b) Various stages of the formation of a "quantum corral" from Fe atoms on a Cu(111) surface [29].

In some cases, Mother Nature actually favors the formation of nanostructures like smooth films, regular nanowire arrays, and ordered quantum dots. Exploiting these situations is called self-assembly. In self-assembled structures, substrate effects or interactions between overlayer atoms or molecules are used to produce nanostructures. One particularly beautiful example of this is seen in the growth of cobalt on the 111 surface of gold [30-31]. This particular crystal face of gold does not have the simple structure that you would find if you terminated its bulk face-centered cubic structure along that crystal plane. It reconstructs into a zig-zag pattern that has been called a “herringbone” structure. The pattern results in regularly spaced atomic kinks on the surface, as shown in Fig. 1.13. When deposited on this surface, Co atoms collect preferentially at those kinks, forming very regularly spaced islands. Another example of self assembly is seen in the co-growth of cobalt and silver on the (110) surfaces of molybdenum [32] or tungsten [33]. Lattice mismatches between the elements are such that it is energetically favorable for the system, when annealed, to separate into alternating Co and Ag stripes that are parallel to the [001] direction.

The way in which material is delivered to a substrate can also have a significant impact on the resulting structures. There are a number of ways to deposit material on a substrate. Atoms of a particular material can be ejected from a source to a target by an incoming stream of inert gas ions. This process, which is heavily used in industry, is called sputtering. This often results in a polycrystalline film and is used for “thick” (> 20 layers) film structures. In molecular beam epitaxy (MBE), a source is heated until it begins to vaporize in vacuum. Vaporized atoms are collected on a nearby substrate. In laser MBE, which is also known as pulsed laser deposition,

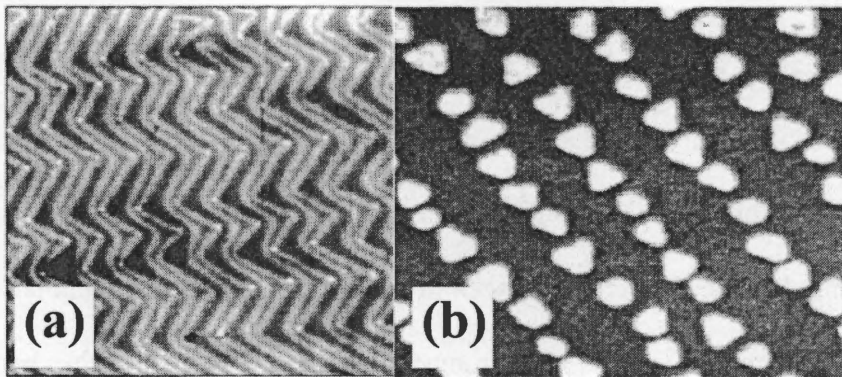


Figure 1.13. Self-assembly of cobalt islands on gold [from ref. 31]. (a) STM image of the famous "herringbone" reconstruction of the Au(111) surface ($730 \times 730 \text{ \AA}^2$). (b) Ordered array of double-layer islands that form when 0.3 atomic layers of Co is evaporated onto this surface ($\approx 800 \times 800 \text{ \AA}^2$).

the target atoms are vaporized by repeated, powerful laser pulses. This results in a large instantaneous flux of atoms. This high flux often means that the films will begin to nucleate in an increased number of places per unit area, resulting in a smooth film. Films can also be grown by electrochemical means, or by spin-coating material from a solution.

Despite the advances that have been made in building magnetic nanostructures, we still have little insight how the magnetic properties of a given material are fundamentally changed as it is confined to the nanoscale along one, two, and three directions. The root of this problem is that it is usually the case that only one type of magnetic nanostructure, whether it is a rough film, a smooth film, nanowire array, or dot assembly, is thermodynamically favored to grow on a given template. In order to grow different types of nanostructures out of a given material, people have therefore had to reach for different substrates. However, since the electronic, magnetic, and structural properties of entities that are made from less than a few layers of atoms are profoundly impacted by the substrates that support them, comparisons between entities grown on different templates do not reveal the *intrinsic* differences induced by nanostructuring. It has been immensely challenging to make direct comparisons of the behavior of various magnetic nanostructures that aren't convoluted by template effects. In chapter 4, we show how this challenge has been met for the case of Fe on the Cu(111) surface. Novel combinations of techniques have been used to produce ultrathin films, nanowire arrays, and quantum dot assemblies from the same amount of the same material on the same substrate.

Many of the approaches for synthesis and characterization require difficult, time-consuming ultrahigh vacuum experiments. For this reason, it is advantageous to be able to look to numerical modeling for guidance. It is certainly easier to repeat calculations with different parameters than it is to repeat UHV experiments. In order to create accurate models of systems, the systems themselves must be thoroughly characterized. This challenge is also addressed in chapter 4. We conduct a combined Monte Carlo / Kerr effect study of Fe quantum dots on Cu(111).

1.3.3 Looking beyond the Mermin-Wagner Theorem

The most basic models of magnetism predict rather boring behavior as the dimensionality of a system is reduced below 3-D. One common way to treat magnetic systems is with the so-called "Heisenberg model", in which individual spins $\vec{S}_i$ and $\vec{S}_j$ are said to interact with each other such that the energy of the system depends on the relative orientation of the spins and on an interaction of strength J_{ij} , which depends on the distance between the spins. The Heisenberg Hamiltonian is usually written as

$$H_{\text{Heisenberg}} = -\frac{1}{2} \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

The interaction J_{ij} can be positive or negative, indicating a tendency toward ferromagnetic or anti-ferromagnetic ordering, respectively, for the spins $\vec{S}_i$ and $\vec{S}_j$. This can be seen by noting that if J_{ij} is positive, the energy of the system is minimized

if the spins with indices i and j are parallel. Likewise, if J_{ij} is negative, the energy is minimized if the dot product between $\mathbf{S}_i$ and $\mathbf{S}_j$ is negative. An often-cited statement of statistical mechanics called the Mermin-Wagner theorem states that there is no long-range order (ferromagnetic or antiferromagnetic) in any 1-D or 2-D Heisenberg model system that has finite-range interactions [34]. This theorem has very recently been strengthened so as to prohibit magnetic order in one- or two-dimensional Heisenberg models with *long-range* interactions that decrease with distance R as $R^{-\alpha}$ if α is sufficiently large [35]. For systems with oscillatory interactions, as in the coupling between spaced magnetic films discussed in section 1.2 (see Fig. 1.7), ferromagnetic long-range order is ruled out at $T > 0$ if α is greater than or equal to 1 in one dimension or if $\alpha > 2.5$ in two dimensions. For systems with monotonically decreasing interactions, ferromagnetic and anti-ferromagnetic long-range order at $T > 0$ is ruled out if α is greater than two times the number of dimensions [35].

Real systems are much more interesting than this. It is even the case that a seemingly ideal two-dimensional lattice, as can be realized in atomically flat single monolayers of iron on the W(110) surface, shows ferromagnetic ordering until it reaches its Curie temperature at 210 K [36]. One fundamental reason that the Mermin-Wagner theorem doesn't work for this system is that we do not have a truly 2-D magnetic system. Since we have supported the magnetic system with a substrate, we have "broken the symmetry" inherent in the 2-D Heisenberg model, so it is no longer really applicable. By saying that we have "broken the symmetry", we mean that we have removed an isotropy that was otherwise present in the system (i.e.

without a substrate, there would be no physical difference between the space above and below the Fe monolayer). Symmetry breaking effects are easy to encounter; they are *always* present in any *real* ultrathin film, nanowire, or magnetic cluster system. For instance, the symmetry of a magnetic system can be broken externally by applying a magnetic field, or by internal factors like the dipolar interaction between moments and magnetic anisotropy, which will be discussed in the next chapter.

The Mermin-Wagner theorem helps us to see why *reduced dimensional magnetism is fundamentally different from bulk magnetism*. In bulk magnets, nearest neighbor exchange interactions alone are enough to stabilize ferromagnetic order. In reduced dimensions, a symmetry-breaking factor or additional interaction is *absolutely essential* to stabilize long-range order. The previous paragraph essentially showed that while the Mermin-Wagner theorem is an important result, it is easy to find loopholes that make it invalid for real systems. People can easily argue, "The Heisenberg model and Mermin-Wagner theorem are too academic to be applied to real systems. Nobody can make true 2-D or 1-D systems and these models leave out too many relevant interactions." That is correct, but then *what are* the relevant interactions that we should be considering? We have to challenge ourselves to look *beyond* the Mermin-Wagner theorem. As in other active areas of condensed matter physics, like the study of superconductivity and colossal magneto-resistive materials, simple textbook theories simply aren't enough to capture the physics that describes how magnetic nanostructures behave.

The magnetism community has made considerable progress in characterization and synthesis of nanostructured materials. The next challenge is to

use these capabilities, perhaps in combination with modeling, in order to gain an understanding of the interactions that occur in artificially structured materials that will allow us to control, or *tailor* their behavior. In the chapters that follow, we will discuss several efforts to accomplish this, and, with the exception of advancing domain imaging technology, attempt to meet the other challenges that we have mentioned in this section.

In chapter 3, we present new approaches for tailoring magnetism in nanostructures. We begin by discussing a study of Co atom-induced spin flop transitions in ultrathin magnetic films. In the study, we identify the relative contributions of the factors that determine the magnetization direction in the films and find a new mechanism for inducing spin-flop transitions that involves changing the arrangement of surface atoms. We follow this with an investigation of how the magnetic ordering temperature of a nanowire array can be tuned by forming the array from an alloy and varying the relative concentrations of the constituents. We end the chapter by showing how magnetic ordering in a “0-D” quantum dot system can be controlled by changing the size and spacing of individual dots. We then demonstrate how this system lends itself to numerical simulations that give us insight toward which interactions are vital in determining the magnetic behavior. In the fourth chapter, we combine our results from these studies of the magnetic dots with previous work in order to study the effect of spatial confinement on a magnetic material. We compare directly the magnetic behavior of 0.8 atomic layers of Fe when grown on a copper surface as films, wires, and dots. In chapter 5 we focus on our work on growth of Fe nanostructures on the insulating NaCl(100) surface [37-38]. Work on

metal-on-insulator systems like this addresses a new challenge. It opens the possibility of exploring how magnetism and electrical current are related in reduced-dimensional nanostructures.

Chapter 2

Concepts in Magnetism and Magnetic Nanostructures

2.1 Introduction

In this chapter, we will introduce the concepts and define many of the terms that will be encountered in later chapters. We begin with a discussion of magnetic anisotropy. This concept is vital since it is a competition among various contributions to the magnetic anisotropy that determines which way the magnetization will tend to point in a magnetic object. This competition is particularly important in two-dimensional ultrathin film systems since reorientations of the magnetization into and out of the film plane, or "spin-flop transitions", are often observed. As we pointed out at the end of the last chapter, magnetic anisotropy plays a large role in permitting the existence of long-range magnetic order in reduced-dimensional systems. We then address the concept of superparamagnetism, which is important when we extend our studies to one-dimensional (nanowire) and zero-dimensional (quantum dot) magnetic systems. Finally, we discuss magneto-optical effects, which we have used to measure the magnetic behavior of all of these types of nanostructures. While familiarity with the concepts in this chapter will be useful for following the discussions in later chapters, experts in the field may wish to skip ahead to Chapter 3.

2.2 Magnetic anisotropy

anisotropic: (adj) Exhibiting properties with different values when measured in different directions.

Magnetic objects tend to be anisotropic in that their magnetization will prefer to point along one direction as opposed to others. This phenomenon can be observed by measuring the hysteresis in the magnetization of the sample as a field is applied along various directions. What one typically finds is that the object will have magnetic **easy axes** and **hard axes**. The difference between the response of a material along an easy axis and the response along a hard axis can be seen in the hysteresis loops in Fig. 2.1. In the curve shown in black in Fig. 2.1, it requires a low applied field, or is “easy”, to drive all of the moments to point along a particular direction. Upon reducing the field to zero, the magnetization remains constant since the moments are quite content to point along this axis. The grey curve in the figure shows that it is “hard” to saturate the moments along the direction perpendicular to the sample. At a relatively large applied field, it is still the case that not all of the moments have been forced to align. Unlike the behavior observed along the easy axis, the magnetization decreases quite significantly as the applied field is reduced to zero, indicating that, in this case, the moments are energetically unhappy to point along the direction in which the field was applied.

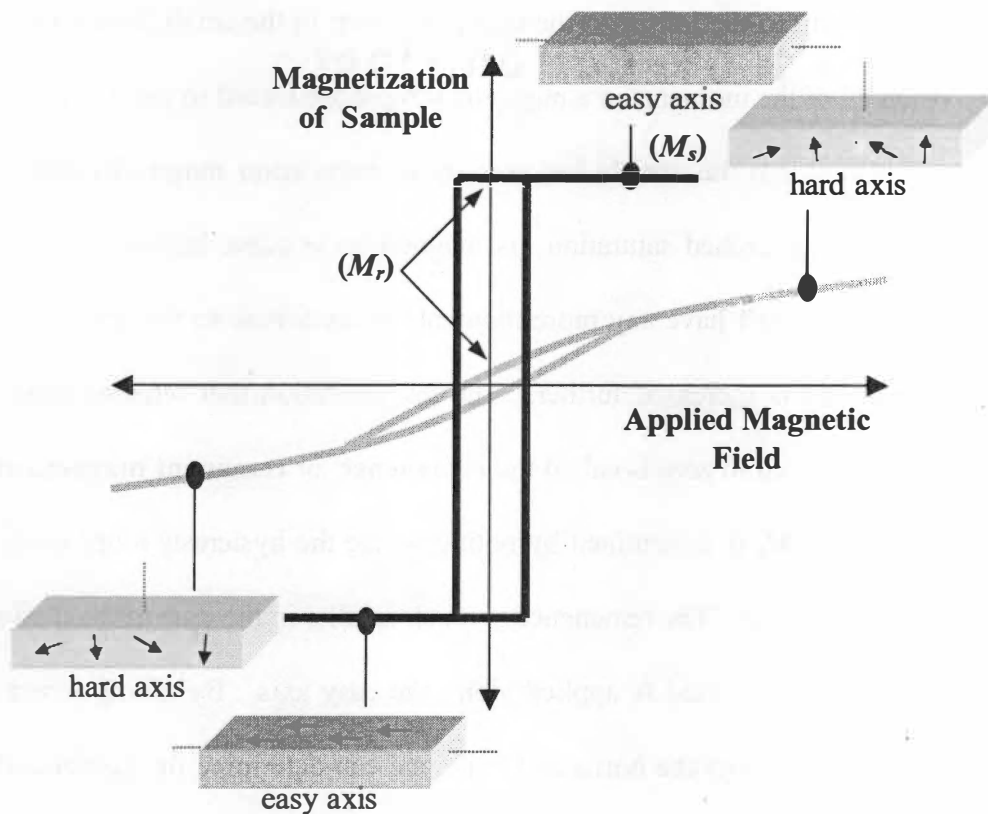


Figure 2.1: Magnetic anisotropy. The dark, rectangular magnetization curve is typical for a material whose magnetization is being driven along an easy axis. A small positive field to get all of the moments in the sample to point along the positive horizontal axis, as shown in the schematic at the top of the figure. The light grey curve shows typical hard axis response. Even with large positive applied fields, the moments cannot be totally aligned in the positive vertical direction.

Before we discuss why it can be easier to magnetize materials in certain directions, we will take this opportunity to use Fig. 2.1 to define a handful of terms that we will often use in the upcoming chapters. The horizontal segments of the black hysteresis loop correspond to situations in which every moment in the sample has been forced to point to the left or to the right, as shown in the small drawings in the figure. When all of the moments in a magnetic sample are forced to point in the same direction, it is said that the sample has reached its **saturation magnetization** (M_s). When a sample has reached saturation, its magnetization curve becomes horizontal since the sample doesn't have any more moments to contribute to the magnetization as the applied field is increased further. The magnetization that remains when the applied field is reduced to zero is called the **remanence**, or **remanent magnetization** (M_r). The value of M_r is determined by noting where the hysteresis loops cross the vertical axis in the figure. The remanence is much smaller in the case of the hard axis loop than it is when the field is applied along the easy axis. By noting where the magnetization curves cross the horizontal axis, one can determine the **coercive field** (H_c), or **coercivity**. These terms refer to the strength of the field that is required to force the net magnetization of the sample to reverse its sign.

2.2.1 *Shape anisotropy*

From experience, most of us know that the magnetization in compass needles and bar magnets lies along their lengths and not across their widths. Far more often than not, the magnetization of a thin film lies in the plane of the film, instead of

perpendicular to it. This effect is called shape anisotropy because it is the physical shape of the magnetic objects that determines to what extent this effect rules the direction of their easy axes.

The underlying cause of **shape anisotropy** is the dipole-dipole interaction. To simply illustrate this point let's consider a system of two point dipoles confined to the endpoints of a rigid stick, as shown in Fig. 2.2. The potential energy between two dipoles can be found in undergraduate texts, and is given by

$$U = \frac{1}{r^3} [\vec{m}_1 \cdot \vec{m}_2 - 3(\vec{m}_1 \cdot \hat{r})(\vec{m}_2 \cdot \hat{r})]$$

or, written in terms of the angles from the figure

$$U = \frac{1}{l^3} [m_1 m_2 \cos(\theta_1 - \theta_2) - 3m_1 \cos(\theta_1) m_2 \cos(\theta_2)]$$

From this expression, we can see that if the dipoles point perpendicular to the stick (for example, at $\theta_1 = \theta_2 = 90^\circ$), the energy of the system is $m_1 m_2 / l^3$. The energy is minimized and is equal to $-2m_1 m_2 / l^3$ when the dipoles point along the length of the stick. Deviations from this configuration cost dipolar energy.

It isn't hard to calculate the energy difference between perpendicular and in-plane magnetized configurations that this dipolar effect causes in ultrathin magnetic films. This is done by summing the interaction energy between each dipole ($\vec{m}_i$) and the field induced by all of the other dipoles ($\vec{H}_{eff}$);

$$E_{shape} = \frac{1}{2} \sum_i \vec{m}_i \cdot \vec{H}_{eff}$$

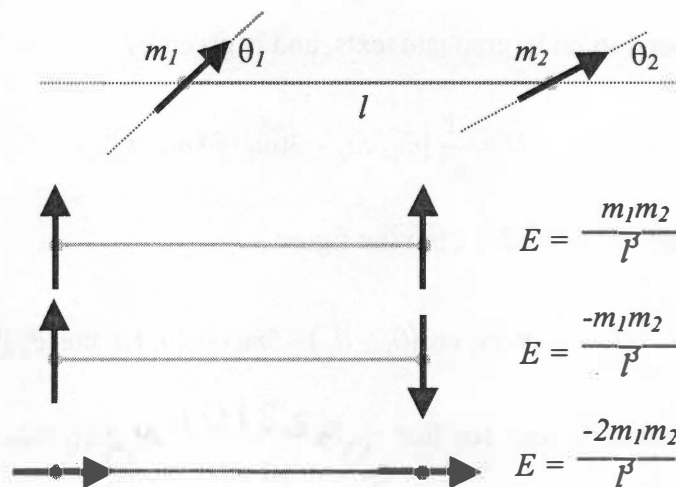


Figure 2.2: The dipole-dipole interaction. It is energetically favorable for dipoles that are confined to a line to orient themselves head-to-tail along the line. This is the origin of shape anisotropy, which dictates that compass needles tend to be magnetized along their length.

The shape effect of the dipolar interaction in thin films can be described in terms of the directional dependence of the "demagnetizing field" that exists in a thin film of magnetic material. If a magnetic field, H , is applied to a thin film, basic electrodynamics tells us that the component of H that is along the surface (tangential H) is continuous across the interface of the film. This means that there is no "demagnetizing field" along the in-plane direction of the film.

The situation is totally different along the direction that is perpendicular to the film. Let's assume that the component of the applied field that is normal to the film is given by H_z^{out} , where the superscript "out" denotes that this is the value of the field in the space outside of the film material. Outside of the material, we have $B_z^{out} = H_z^{out}$, as shown in Fig. 2.3. Basic electrodynamics tells us that the component of B perpendicular to the film is continuous across the interface, so $B_z^{in} = B_z^{out}$. From the general relationship between B and H , we know $B_z^{in} = H_z^{in} + 4\pi M_z$, in which M_z is the component of the magnetization of the film along the z -direction. Combining the above results gives $H_z^{in} = H_z^{out} - 4\pi M_z$, which tells us that there is a field along the negative z -direction of magnitude $4\pi M_z$ that opposes the applied field.

We can now calculate the interaction of the dipoles in the film with this demagnetizing field. This is given by

$$E_{shape} = \frac{1}{2} \sum_i \vec{m}_i \cdot \vec{H}_{demag}$$

If the film is uniformly magnetized, we have

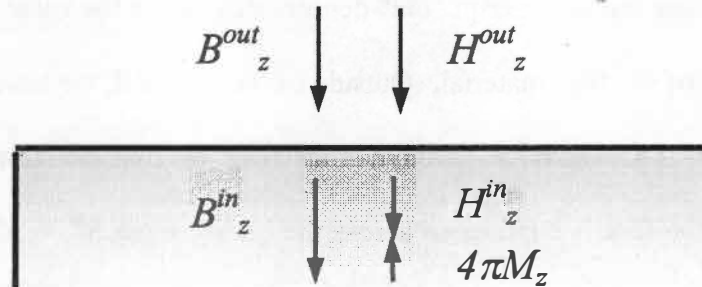


Figure 2.3: The demagnetizing field. In a flat film, a "demagnetizing field" of magnitude $4\pi M_z$, where M_z is the z -component of magnetization of the sample, opposes a field that is applied perpendicular to the sample. As shown in the text, this effect results in a contribution toward the anisotropy energy of the sample of the form $2\pi M^2 \cos^2(\theta)$, where M is the magnitude of the sample magnetization and θ is the angle between the magnetization and the surface normal. This term causes the magnetization to prefer to lie in the plane of a flat film.

$$EV = -\frac{1}{2} \iiint \vec{M} \cdot \vec{H}_{demag} dV = -\frac{1}{2} \iiint \vec{M} \cdot (-4\pi\vec{M} \cos(\theta)\hat{z}) dV$$

where V is the volume of the film. Finally, we find that the energy per unit volume is

$$E_{shape} = 2\pi M^2 \cos^2(\theta)$$

This expression shows that it is energetically favorable for the magnetization to point along $\theta = \pi/2$ or $3\pi/2$, which is *in the plane* of the film.

2.2.2 Magneto-crystalline anisotropy

It is, however, not always the case that the magnetization in a thin film points along its flat dimension instead of in the perpendicular direction. Just one example of deviation from this behavior is found in the ultrathin Fe/Cu(100) system, whose magnetic phase diagram is shown in Fig. 3.1 in Chapter 3. Other systems that show perpendicular magnetization include Co/Au [1] and Fe/W [2]. It is clear that in these systems, another factor is competing with the dipolar interaction.

This factor is the magnetocrystalline anisotropy. This anisotropy results from interactions between spins and the asymmetric environment created by the crystal lattice of the material. A simple way to picture this effect is shown in Fig. 2.4. It is not difficult to imagine that there could be a difference in energy between the situations in which the magnetization points in the direction indicated by the dotted arrow and

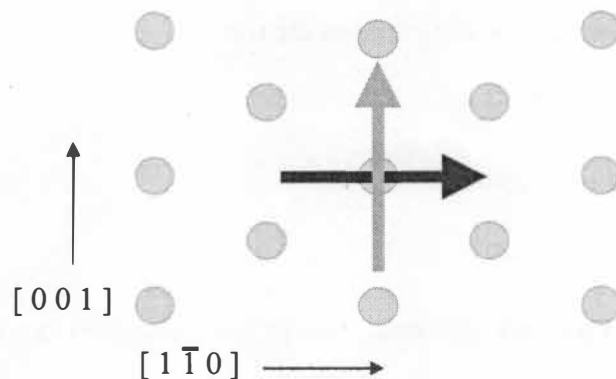


Figure 2.4: An example of magnetocrystalline anisotropy. The atoms in single atomic layer of iron on the W(110) surface assume bcc(110) arrangement of the substrate. A top view of this arrangement is shown by the grey spheres in the picture above. The $[1\ 1\ 0]$ direction points into the page. When iron is grown on this surface, its easy axis of magnetization lies along the $[1\ -1\ 0]$ direction. The $[0\ 0\ 1]$ direction is a hard axis. The difference is due to the fact that the atomic arrangement is different along these two crystallographic directions. One difference is that the lattice spacing is $a\sqrt{2}$ along the easy axis and a along the hard axis. ($a = 3.158\ \text{\AA}$). This relationship between magnetic behavior and atomic structure is called magnetocrystalline anisotropy.

along the direction indicated by the solid arrow, due to the differences in the symmetry of the host lattice along those directions.

2.2.3 Phenomenological treatment of anisotropy in thin films

In the following, we will introduce anisotropy constants and a phenomenological model that is typically used to treat magnetism in ferromagnetic thin films and multilayers [3-4]. The model is important because it can be used to predict conditions under which a magnetic film might, for example, undergo a magnetization reorientation transition. This model will be particularly important in Chapter 3, when we use it to characterize the spin reorientation in cobalt-capped iron films on copper. Later we find that this model is inadequate in that it considers only the amounts of material that make up the film and capping layer, but not their specific atomic arrangement.

For most objects, a description of the magnetic anisotropy will be extremely complicated since it has to account for the orientation of the magnetization and surface planes relative to the crystallographic axes. In thin films, it turns out that a very simple ansatz [3-4] is sufficient;

$$E = K^{\text{eff}} \sin^2(\theta)$$

In this equation, the energy of the system (E) is determined by the angle (θ) between the magnetization and the film normal and the strength of the anisotropy of the system (K^{eff}). (This expression is actually more than an ansatz; it can be thought

of as the first term in a series expansion of the energy in even powers of the sine function. Only the *even* powers are kept since there is usually no physical reason for it to be energetically different for the magnetization to point *into* the sample along the normal or *out of* the sample along the normal.) The constant K^{eff} is called the effective anisotropy constant, and depends on the film thickness and the temperature of the system. One can easily see that if K^{eff} is positive, the magnetization of the system will prefer to be perpendicular to the film plane. Conversely, the energy will be minimized when M lies parallel to the plane if K^{eff} is negative [5]. When the film thickness or temperature is changed such that the effective anisotropy passes through zero, a spin flop transition (from perpendicular to in-plane, or vice-versa) will occur.

A large body of work has empirically shown that the effective anisotropy can be broken into a contribution from the volume, or bulk of the film (K_v) and a contribution from the surfaces (K_s) that, as one might expect, becomes less important as the film thickness increases [4]. This is written as $K_{eff} = K_v + 2K_s/t$. Multiplying both sides of the equation by the thickness of the film (t) gives $K_{eff}t = K_v t + 2K_s$, which shows that a plot of $K_{eff}t$ vs. t yields a straight line, from which the slope can be used to determine the volume contribution (K_v) and the y -intercept is twice the surface anisotropy (K_s). A plot for the case of cobalt/palladium multilayers is shown in Fig. 2.5. As described in [3], the negative slope means that K_v is negative and favors in-plane magnetization. The positive intercept shows that the surface anisotropy competes with K_v since it is of the opposite sign. When the film thickness becomes large enough, the quantity K_v outweighs the combination $2K_s/t$ and, as can be seen in

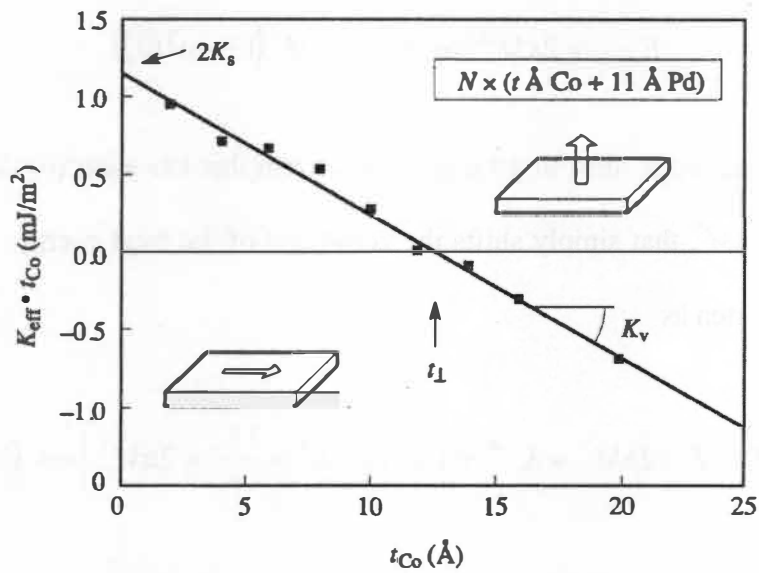


Figure 2.5: Separating the surface and volume contributions to magnetic anisotropy [from ref. 4]. The plot shows the product of the magnetic anisotropy energy and film thickness versus the film thickness. The y-intercept equals twice the surface anisotropy energy and the slope gives the volume anisotropy constant.

the expression for K_{eff} above, the effective anisotropy constant changes sign. At this point, a spin-flop transition occurs, as seen in the figure.

Here, the volume anisotropy constant is negative primarily because it includes shape anisotropy. We can separate the shape anisotropy contribution -- and it is wise to do so since this part can be calculated exactly. The key is to notice that the shape anisotropy term can be rewritten like this:

$$E_{shape} = 2\pi M^2 \cos^2(\theta) = 2\pi M^2 (1 - \sin^2(\theta))$$

This shows that the shape anisotropy introduces a term that has a $\sin^2(\theta)$ dependence and a constant, $2\pi M^2$, that simply shifts the zero-level of the total energy. The total energy is now written as

$$E' = E - 2\pi M^2 = K'_{eff} \sin^2(\theta) = \left(K'_v + \frac{2K_s}{t} - 2\pi M^2 \right) \sin^2(\theta)$$

K'_v is a new volume anisotropy constant that does not include the shape anisotropy.

The condition for spin reorientation is now satisfied when

$$K'_v + \frac{2K_s}{t} = 2\pi M^2,$$

or when the shape anisotropy, which tends to force the magnetization to lie in-plane, is balanced by the surface and volume anisotropies, which may oppose the shape anisotropy and favor a perpendicular easy axis.

As mentioned previously, the factor of 2 in the surface anisotropy term comes from the fact that a free or embedded film has two identical surfaces. In more complicated structures with dissimilar surfaces, the anisotropies shown in the expression above must be modified accordingly. We end this introduction to magnetic anisotropy by showing how anisotropy constants and the condition for spin reorientation could be applied to the realistic system shown in Fig. 2.6. We treat the terms in the spin-reorientation equality

$$K'_v + \frac{2K_s}{t} = 2\pi M^2,$$

from left to right.

In the case of the system shown in the figure, the volume anisotropy must consist of two terms since we now have two magnetic materials. This term is now a weighted average of the volume anisotropies of the film and cap materials. It can be written like this:

$$K'_v \Rightarrow \frac{K_v^{film} d_{film} + K_v^{cap} d_{cap}}{d_{film} + d_{cap}}$$

Likewise, we have to define new anisotropy constants for each type of interface in the problem. First, we have the film-substrate interface anisotropy ($K_s^{film-sub}$), which must be weighted by a factor of one since there is one full interface between the film and substrate. The film-cap interface introduces an anisotropy constant given by $K_s^{film-cap}$ that is weighted by a factor of ϕ^{cap} since this fraction of an

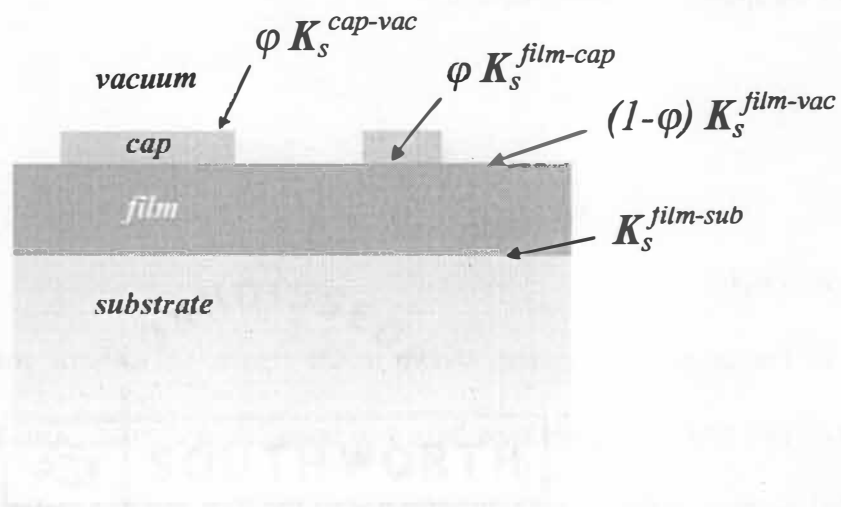


Figure 2.6: How to assign anisotropy constants to a magnetic multilayered system. Only the surface anisotropy constants and weighting factors are shown. The magnetic cap and magnetic film are also assigned volume anisotropy constants, which are K_v^{cap} and K_v^{film} respectively. In the figure, the cap covers a fraction ϕ of the film surface. This leaves a fraction $1-\phi$ of the film surface exposed to the vacuum. This is why the anisotropy constant for the film-vacuum interface is weighted by a factor of $1-\phi$.

atomic layer is taken up by that interface. Similarly, the film-vacuum interface contributes an anisotropy of $K_s^{film-vac}$ that is multiplied by a factor of $1-\phi^{cap}$. Finally, the cap-vacuum interface contributes an anisotropy energy of $\phi^{cap}K_s^{cap-vac}$. In all of its glory, this second term looks like this:

$$\frac{2K_s}{t} \Rightarrow \frac{K_s^{film-sub} + \phi^{ccap} K_s^{film-cap} + (1 - \phi^{cap}) K_s^{film-vac} + \phi^{cap} K_s^{cap-vac}}{d_{film} + d_{cap}}$$

Similarly, we use a weighted average of the magnetizations of the two magnetic constituents in the third term. The shape anisotropy term becomes:

$$2\pi M^2 \Rightarrow 2\pi \left(\frac{M_{film} d_{film} + M_{cap} d_{cap}}{d_{film} + d_{cap}} \right)^2$$

The condition for spin reorientation is met at the thickness and temperature when the sum of the first two terms is equal to this last term. The challenge, of course, becomes gathering enough information to be able to identify each of the unknown bulk and surface anisotropy constants. We tackle this problem in Chapter 3 when we discuss cobalt capping-atom-induced spin-reorientations of Fe films on the Cu(100) surface.

2.3 Magnetic viscosity and superparamagnetism

Superparamagnetism [6-8] is the name given to the behavior of a collection of single-domain magnetic particles that do not interact with each other. It is an

important first approximation to make in predicting how a system of isolated magnetic quantum dots is going to behave. In this section, we will describe the origins of superparamagnetism and how these systems behave. We begin with a brief review of the general classes of magnetic materials so that the unique features of superparamagnetism can be emphasized.

There are five general ways in which the magnetic moments of materials respond in the presence (and sometimes in the absence) of magnetic fields. In **diamagnets**, the electrons respond via Lenz's Law so as to oppose an applied magnetic field. This can be seen in Fig. 2.7(a). When an upward magnetic field is applied to the atom shown in the figure, the electron path takes on a more clockwise (when viewed from above) sense in order to oppose the additional flux through the orbit. In a material, this results in a reduction of the moment per atom along the direction of the applied field. In **paramagnets**, the individual spins follow the applied field in slavlike fashion. As the applied field is increased, more and more spins align. In **ferromagnets**, the individual spins become spontaneously ordered along the same direction as their neighbors below a certain temperature called the Curie temperature, as shown in Fig. 2.7(c). The spins order directionally opposite to their neighbors below the so-called Neel temperature in **anti-ferromagnets**. **Ferrimagnets** are exactly like anti-ferromagnets, except for the fact that the anti-aligned spins don't exactly cancel each other, leaving a net moment.

As the name implies, superparamagnetic systems are similar to paramagnets. The similarity is found in that they are built of non-interacting spins that tend to follow an applied magnetic field as its strength is increased. The first major

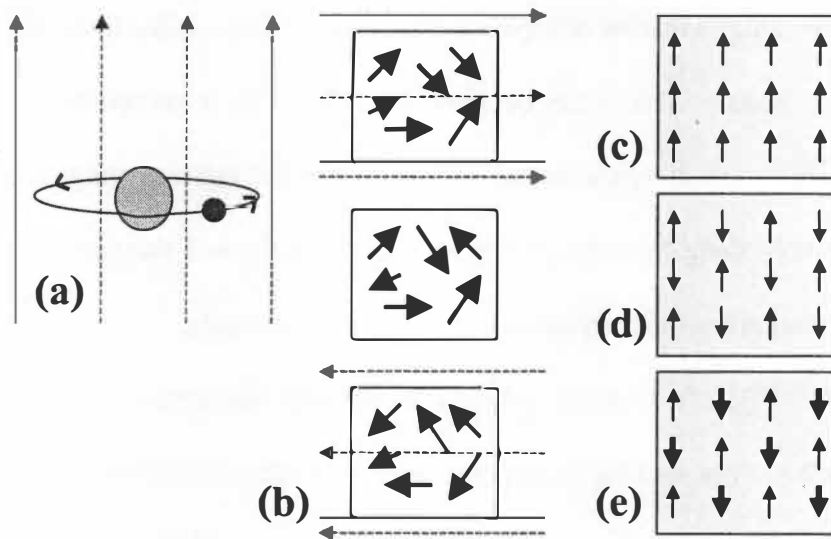


Figure 2.7: Five classes of magnetic materials. (a) In diamagnets, the motion of the electrons tends to produce a field that opposes any applied field that creates flux through their orbits. (b) In paramagnets, the moments tend to follow the applied field. When no field is applied (center), the moments are randomized and net magnetic moment is zero. (c) In a ferromagnet, neighboring moments tend to be parallel to each other when the temperature is low enough, even in the absence of an applied fields. (d) In an anti-ferromagnet, neighboring moments tend to be anti-parallel when the material is below its Neel temperature. The net moment is zero when no field is applied. (e) A ferrimagnet shows anti-ferromagnetic order but the net moment is non-zero due to two different species of moments that do not cancel each other out.

difference is that the relevant moments in superparamagnetic systems are not those of single atoms, but rather those of a single domain ferromagnetic particle made up of ~ 1000 atoms. In a way, superparamagnets are artificial paramagnets in the same sense that multilayered FM films can be artificial anti-ferromagnets. In each case, the fundamental spins are spin blocks, rather than individual atoms.

The most unique feature of superparamagnetic systems is the time dependence of the magnetization. This time dependence is due to a competition between anisotropy energy, which tends to encourage moments that are magnetized in a particular direction along the easy axis to remain that way, and thermal fluctuations, which tend to randomize the orientations of the particle moments.

As in ref. [6], let's consider a system of isolated, non-interacting particles, as shown in Fig. 2.8. The system is prepared such that the magnetic easy axes of the particles are aligned with each other. The relevant energies in the system include $-\mu H \cos(\theta)$, which is the energy of the interaction of a dipole moments, μ , that is canted at an angle θ from an applied H field. This term tends to align each moment with the applied field. A second important contribution is made by the anisotropy energy, $KV \sin^2(\theta)$, which says that there is an energy barrier of strength KV that must be overcome to rotate a moment from one orientation along the easy axis to the other. The third relevant energy in the problem is the thermal energy, $k_B T$.

Suppose we then saturate the moments by applying a large magnetic field, and then abruptly remove the field, allowing the system to relax. To reach thermal equilibrium, which means a state of zero net remnant magnetization, a sufficient

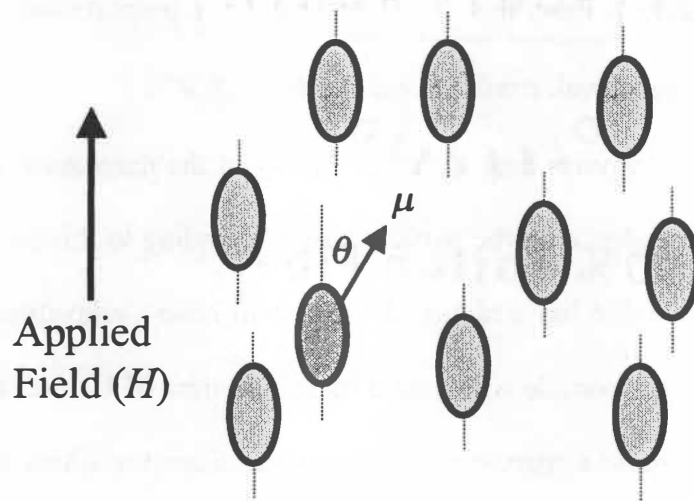


Figure 2.8: A system of isolated, non-interacting magnetic particles. They each have a magnetic moment μ and their easy axes are all oriented in the same direction. In the absence of an applied magnetic field, H , the only relevant energies in the system are the anisotropy energy, which tries to keep the moment pointing up or down along the easy axis, and the thermal energy, $k_B T$.

number of moments must be reversed by thermal activation over the anisotropy barrier. From statistical mechanics, we know that the likelihood of these reversals is proportional to $e^{-\text{energy barrier} / k_B T}$, or $e^{-KV / k_B T}$. The decay rate, $1/\tau$, over which the magnetization decays will, of course, be directly proportional to this probability. (If the probability for a fluctuation to occur is high, the rate at which the moments randomize will be high.) From this, it follows that $1/\tau$ is proportional to $e^{-KV/k_B T}$ and that the remanent magnetization will vanish like $M_r = M_s e^{-t/\tau}$.

The important physics here is that the decay of the magnetization has a very strong and clear dependence on the particle size. According to this simple model, a spherical iron particle that has a radius of 115 Å will have a relaxation time of 10^{-1} seconds, while a 150 Å particle will have a relaxation time of 10^9 seconds [6]. This means that there is quite a narrow range of particle sizes for which the relaxation times can be conveniently observed. Above a certain radius and below a certain temperature, the magnetization decays so slowly that it can, for all practical purposes, be considered to be stable. Such a system is said to have a high **magnetic viscosity**. On some level, a system with a high magnetic viscosity is difficult to distinguish from a ferromagnet. One observes hysteresis if the time that it takes to sweep an applied field is much lower than the relaxation time.

Because of the connection between relaxation time and temperature, it is useful to characterize a system by defining a "blocking temperature" at which the relaxation time is 100 seconds. Below the blocking temperature, the net moment takes longer than 100 seconds to decrease to $1/e$ of its saturation value. The spins are said to be "blocked" from relaxing to thermal equilibrium by the anisotropy barrier.

To be rigorous, superparamagnetism typically refers to the behavior that is observed well above the blocking temperature, and for particles that are so small that the anisotropy barrier is small enough to allow several thermally activated flips to occur between measurement. In this regime, systems of non-interacting particles show absolutely no hysteresis and magnetization vs. H/T curves that are recorded at different temperatures map directly onto each other [6].

Finally, we mention that the simple exponential model captures the basic physics of non-interacting particles, but is actually not typically used to describe experimental results. This is because particles in real systems do not have perfect, delta-function size distributions. This means that in real systems, there is a considerable distribution in particle relaxation times. Because of this, it has been argued that the decay cannot be a simple exponential. The function that is of most widespread use in fitting experimental data is $M_r(t) = C - S \ln(t/t_0)$. Despite its popularity, this function has been described as "unphysical", "inconvenient", "completely arbitrary", and even "meaningless" for a number of reasons that are spelled out in ref. [8].

2.4 Magneto-optical effects

2.4.1 Introduction

In the middle of the 1800s, it was discovered that if linearly polarized light is incident upon a material in a magnetic field, both the transmitted and reflected beams

undergo a small polarization rotation and can pick up ellipticity. The response of the transmitted light is said to be due to the Faraday effect, in honor of Michael Faraday who reported the phenomenon in 1845. The change in the reflected beam became known as the Kerr effect, after John Kerr observed it thirty years later [9-10].

Over the past two decades, these magneto-optical effects have seen a tremendous growth in their importance to mankind. The Kerr effect is the key physical principle used in high density information storage devices called "M-O disk drives" that, until a recent decline in popularity in favor of other non-magnetic disks, were commonly found in personal computers. In 1985, the effect was incorporated into a technique for studying surface magnetism that was given the catchy acronym SMOKE, which stands for the Surface Magneto-Optical Kerr Effect [11]. With the SMOKE, it is rather easy to detect the magnetic response of sub-monolayer amounts of material, making it, along with the STM, one of the most vital approaches for studying magnetic nanostructures.

In the sections that follow, we will discuss the physical origins of magneto-optical effects. Practical details relating to the use of the SMOKE technique are presented in the Appendix to this dissertation.

2.4.2 The macroscopic origin of magneto-optical effects.

To understand the Faraday and Kerr effects, it is necessary to understand linear and circular-polarized light. A linearly polarized light wave that travels in the z direction can be thought of as being made up of two electromagnetic waves whose

electric vectors oscillate along the x and y direction exactly in phase with each other. As is shown in Fig. 2.9, circularly polarized light is almost exactly the same, except for the fact that the two constituent waves should be exactly $1/4$ cycle out of phase with each other. Linearly polarized light can also be thought of as being made up of two equal contributions of circularly polarized light of opposite handedness. If a light wave has an excess of either right or left circular light, than it becomes something between linear and circular; elliptical light.

Now lets consider what happens to linearly polarized light, which, again, can be thought of as being composed of equal parts right and left circular light, if it was sent into a medium that responded differently to right-handed light than it did to left-handed light, such that it varied the relative contribution of each to the composite wave. In this case, the light wave would pick up rotation and ellipticity as observed in the Faraday and Kerr effects.

The conductivity tensor, σ , relates the current density, $\mathbf{J}$, in a material to the electric field, $\mathbf{E}$, through Ohm's relation $\mathbf{J} = \sigma \cdot \mathbf{E}$. In Cartesian coordinates, we have

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

The elements along the diagonal are rather intuitive. For instance, an electric field along the x direction in a conductor leads to a current density along the x direction. Some materials have significant off-diagonal contributions to the conductivity tensor.

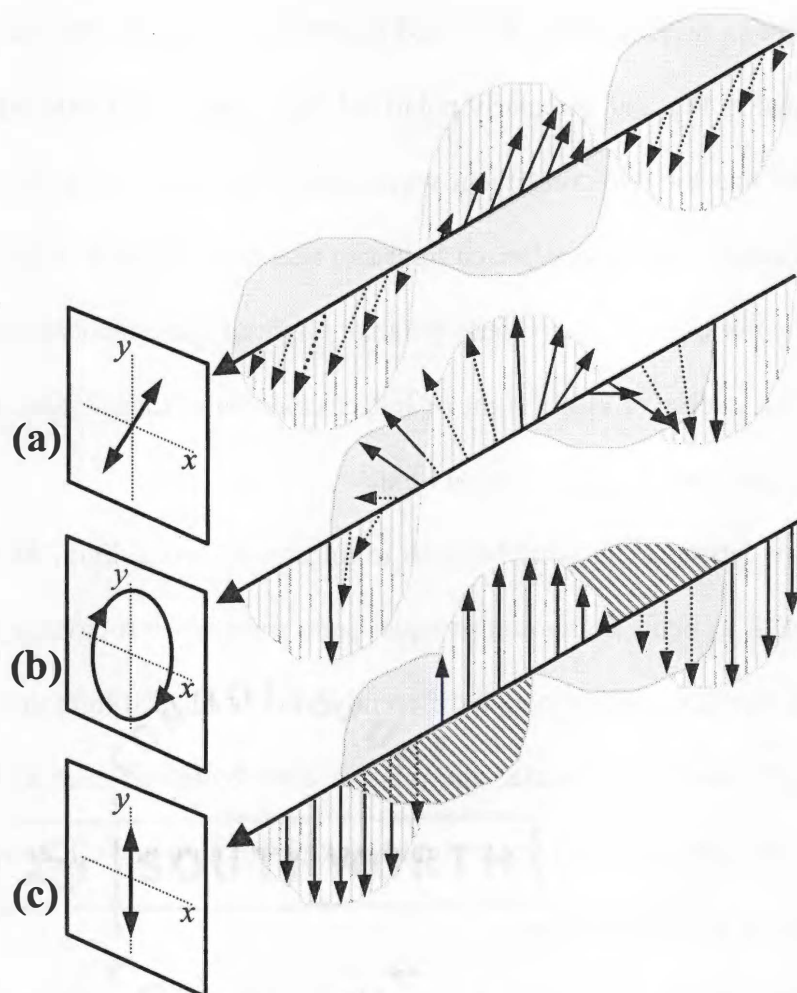


Figure 2.9: Linear and circularly-polarized light. (a) The diagonal arrows indicate the magnitude and direction of the electric field of the wave that results from combining two waves that travel in the positive z direction and have electric vectors that oscillate in phase with each other and in the x and y directions respectively. In this case, the electric vector of the composite wave is confined to a line, as shown in the "screen" in front of the incoming wave. This is linearly polarized light. (b) When the x and y waves are out of phase with each other by a quarter cycle, the electric vector of the composite wave is found to trace out a circle. This is circularly polarized light. In this case, the x component leads the y component by $1/4$ cycle and the light is said to be "left-handed". If the x component lagged the y component by $1/4$ cycle, the electric vector would be found to trace out a circle in the opposite direction and the light would be "right-handed". (c) If right- and left-handed light were combined such that their y components were in phase, this wave, which is linearly polarized along the y direction, would result. This is because the x components would cancel each other, as shown in the figure. All linearly polarized light can be thought of as being composed of right- and left-circular light in this way.

In the following, we will show that these off-diagonal elements lead to different indices of refraction for right- and left-circular light in a medium, and are thus responsible for magneto-optical effects.

As an ansatz, let's assume that the conductivity of a material has two non-zero off-diagonal elements and is of the following simple form:

$$\sigma = \begin{pmatrix} \sigma_0 & -\sigma_1 & 0 \\ \sigma_1 & \sigma_0 & 0 \\ 0 & 0 & \sigma_0 \end{pmatrix}$$

Two relevant Maxwell Equations are

$$\nabla \times E = -\frac{1}{c} \frac{\partial H}{\partial t}$$

and

$$\nabla \times H = \frac{1}{c} \frac{\partial E}{\partial t} + \frac{4\pi}{c} \sigma \cdot E$$

in which Ohm's relation has been used to express the last term as a function of the electric field instead of the current density. Taking the curl of both sides of the first Maxwell equation gives the following wave equation for the electric field

$$\nabla \times \nabla \times E = -\frac{1}{c} \frac{\partial(\nabla \times H)}{\partial t} = -\frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} - \frac{4\pi}{c^2} \sigma \cdot \frac{\partial E}{\partial t}$$

For a light wave propagating along the z direction, we can express the electric field as

$$E = \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} e^{i\omega t - \frac{i\omega N}{c} z}$$

Direct substitution of this expression for the electric field into the wave equation gives

$$\begin{pmatrix} \frac{\omega^2 N^2}{c^2} E_x \\ \frac{\omega^2 N^2}{c^2} E_y \\ 0 \end{pmatrix} e^{i\omega t - \frac{i\omega N}{c} z} = -\frac{(i\omega)^2}{c^2} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} e^{i\omega t - \frac{i\omega N}{c} z} - \frac{4\pi}{c^2} \begin{pmatrix} \sigma_0 E_x - \sigma_1 E_y \\ \sigma_1 E_y - \sigma_0 E_x \\ \sigma_0 E_z \end{pmatrix} e^{i\omega t - \frac{i\omega N}{c} z}$$

If we just focus on the x and y components of the electric field, we find that they are related by the two equations

$$\begin{aligned} (A_0 - N^2)E_x - A_1 E_y &= 0 \\ A_1 E_x + (A_0 - N^2)E_y &= 0 \end{aligned}$$

in which

$$\begin{aligned} A_0 &= 1 + \frac{4\pi}{i\omega} \sigma_0 \\ A_1 &= \frac{4\pi}{i\omega} \sigma_1 \end{aligned}$$

It is important to note here that the constant A_I contains only the contribution from the *off-diagonal* elements of the conductivity tensor. In order for the two equations for the x and y components to have a non-trivial solution, the determinant of coefficients must vanish, so we find, finally, that

$$(A_0 - N^2)^2 + A_I^2 = 0$$

There are two solutions to this equation, which tell us that there are two modes for the light wave in the medium. The first solution has an index of refraction given by $N^2 = A_0 - iA_I$ and electric field components related by $E_y = iE_x$. The second solution has a refractive index given by $N^2 = A_0 + iA_I$ and fields $E_y = -iE_x$. Respectively, these are right-handed and left-handed circularly polarized light waves with different indices of refraction, which means that this medium will show magneto-optical activity. From this development, it is evident that if the off-diagonal elements of the conductivity tensor were zero (and therefore the constant A_I was zero) then the solutions wouldn't be circularly polarized and would not have differing indices of refraction.

2.4.3 Microscopic origins of the Kerr effect

Here is the simplest explanation of why one observes a rotation in the polarization of light as is reflected from a magnetized material. The electrons in the material respond to the oscillating electric field of the incident light wave by accelerating back and forth. This motion is deviated by the Lorentz force provided by

the field that is due to the magnetization of the medium. This deviation contributes to the outgoing lightwave, and the plane of polarization of the reflected light is rotated relative to that of the incoming wave.

This simple picture works well to describe the weak Kerr rotation observed in paramagnetic materials. Unfortunately, this picture doesn't work at all in explaining the relatively enormous Kerr response observed in light reflected from ferromagnetic materials. Within this model, a comparison of the Kerr rotations suggests that the effective magnetic field inside of a ferromagnet is 10^5 times higher than it is in paramagnets. There is no other physical evidence to suggest that magnetic fields of that magnitude exist in ferromagnets. Because of this, people have been forced to search for other models to explain this behavior.

A real, microscopic explanation of magneto-optical effects in ferromagnetic materials was initiated by Hulme in 1932 and completed as the Ph.D. thesis of Petros Argyres in 1955 [11]. In a nutshell, Argyres showed that including the interaction between an electron and an effective field that it "feels" as it moves through a material lead to non-zero off-diagonal elements in the conductivity and polarizability tensors that determine the index of refraction. (For brevity, I did not include contributions from the polarizability tensor in the previous section.) As this calculation itself made up a significant part of a Ph.D. thesis, we will just highlight important details here, and will end the discussion with an atomic view of the mechanism of the Kerr effect that is somewhat easier to visualize.

The key step that was taken by Hulme and Argyres was the inclusion of a "spin-orbit" term which considered the interaction between the magnetic moment, μ ,

of an electron with the effective magnetic field that it feels as it moves with momentum p through an electric field, $-\nabla V$, inside of a material. Argyres began with a one electron Hamiltonian that had three terms. The Hamiltonian was $H = H_0 + H^I + H^{II}$ in which

$$H_0 = \frac{\vec{p}^2}{2m} + V(r)$$

$$H^I = \frac{1}{2m^2c^2} (\nabla V(r) \times \vec{p}) \cdot \vec{s}$$

$$H^{II} = \frac{e}{mc} \vec{A}(r, t) \cdot \vec{p}$$

The first term contains the kinetic energy of the electron and the electrostatic potential of the crystal. The third term, H^{II} describes the interaction between the magnetic vector potential, A , of a monochromatic light wave and an electron. The second term, H^I is the important new "spin-orbit" term. Its meaning can be understood by comparing its form to that of H^{II} . Via vector identities, H^I can actually be re-written as

$$H^I = \frac{1}{2m^2c^2} (\vec{s} \times \nabla V(r)) \cdot \vec{p}$$

By comparing this to H^{II} , it is evident that the cross product of the electron spin operator, s , and the electric field, $-\nabla V$, provide an effective magnetic vector potential that interacts with the momentum of the electron.

Argyres proceeded to use this Hamiltonian in Schrödinger's equation to find the electron wavefunctions, which he then used to calculate the current density. With

the current density, he found the components of σ , the conductivity tensor and α , the polarizability tensor, via the relation

$$\vec{J} = \sigma \cdot \vec{E} + \alpha \cdot \frac{\partial \vec{E}}{\partial t}$$

The calculation showed that these tensors had non-zero off-diagonal elements which came directly from the new spin-orbit term. Knowledge of these tensor elements allowed him to calculate the difference in the index of refraction in right- and left-circular modes explicitly, in a way similar to that shown in the previous section.

Argyres' calculation gives an explanation, within the band theory of solids, why magneto-optical effects are observed. It is perhaps easier to view the microscopic origins of these effects with a model involving a single atom. In the following, we will look at the atomic energy levels within a single transition metal and see why, in ferromagnetic materials, there is a difference in how right- and left-circular light is absorbed.

In atoms, electronic states are characterized by quantum numbers n , l , m_l , and m_s . For dipolar transitions between these states, there are selection rules which restrict allowable transitions to those for which the change in the l and m_l quantum numbers is ± 1 . A transition in which Δm_l is $+1$ involves absorption of left circular light and a transition in which Δm_l is -1 corresponds to an excitation from a right-circular wave. Given the selection rules, transitions between the degenerate d_{xz} and d_{yz} levels ($l = 2$, $m_l = \pm 1$) and a p_z level ($l = 1$, $m_l = 0$) are allowed.

The upper half of Fig. 2.10 is a sketch of this transition in a paramagnetic $3d$ transition metal (like Cu). The imbalance in the way in which spin up electrons absorb the two types of circular light is exactly offset by the way in which spin down electrons absorb light. Figure 2.10 also shows how the same transitions would occur in a ferromagnetic $3d$ transition metal (like Co). Ferromagnets are different from paramagnets in that the spin-up and spin-down d electron levels become significantly separated in energy due to the exchange interaction. Consequently, as shown in the figure, there is a major imbalance in the way in which the material absorbs right- and left- circular light. This figure provides a simple picture of the microscopic origin of magneto-optical effects.

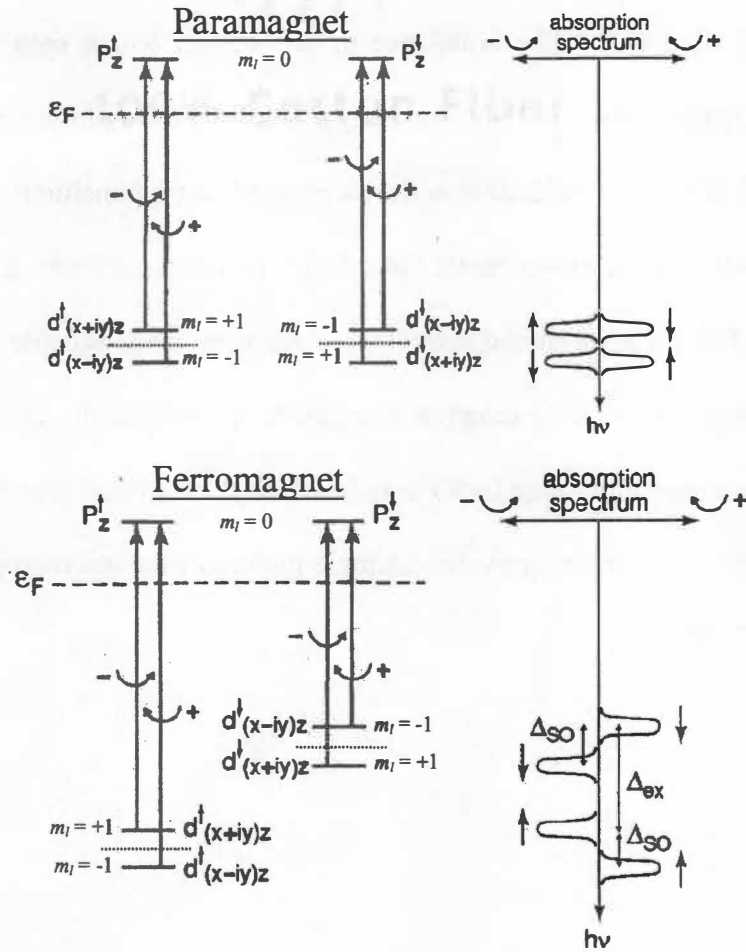


Figure 2.10: An atomic picture of the Kerr effect [adapted from ref. 13]. The interaction between an electron's orbital angular momentum, L , and its spin, S , can shift electron energy levels by an amount proportional to $L \cdot S$. This means that states that have different values of the quantum number m_l , which gives the z -component of L , will be shifted in energy relative to each other. This interaction causes the energy of spin-up states to be raised if they have $m_l = 1$ (since L would be parallel to S) and to be lowered if they have $m_l = -1$ (since L would be anti-parallel to S), as shown in the figure above. The reverse is true for spin-down electron states. The top figure shows how this interaction splits degenerate d -states in a paramagnetic transition metal. The splittings are symmetric for spin-up and spin-down states such that right and left circularly polarized photons are absorbed equally by the atom. The bottom figure shows this same spin-orbit splitting combined with the so-called exchange splitting that lowers the energies of spin-up states and raises the energies of spin down states in ferromagnets. In this case, the transitions for right ($\Delta m_l = -1$) and left ($\Delta m_l = +1$) circular light do not occur at the same energies. This difference in absorption for right and left circular light is the origin of the Kerr effect.

Chapter 3

New Approaches for Tailoring Magnetism

3.1 Films: controlling magnetic anisotropy via placement of added atoms

The experiments that we present in this section show that the magnetization direction of ultrathin films can be controlled, or forced to re-orient to and from the film normal and in-plane directions, by adding atoms of another magnetic material. We exercise this control in a magnetic system that, as we will show momentarily, has been of tremendous importance to the thin-film magnetism community. By controlling the direction of the magnetic easy axis in this system, we have been able to identify the relative contributions of factors that determine its anisotropy. These factors include the anisotropy induced by the various interfaces in the system. Most importantly, we have discovered that changing the arrangement of the added atoms can also induce a spin reorientation. This phenomenon is not predicted by the established, empirical model that is typically used to describe magnetic ultrathin films. As discussed in the previous chapter, the model considers only the amount of added material, and not how it is configured.

3.1.1 Introduction to face-centered cubic iron on Cu(100)

In our discussion of magnetocrystalline anisotropy in the last chapter, we saw one way in which the crystal structure of a material can affect its magnetic properties. The magnetic properties of iron, when prepared in the face-centered cubic (fcc) phase, are extremely sensitive to the atomic arrangement. Electronic structure calculations predict a myriad of possible magnetic phases for fcc iron, which range from non-magnetic and anti-ferromagnetic to ferromagnetic [1-2]. These phases are sensitive to the atomic spacing and volume of the fcc unit cell, and were calculated to be separated very little in energy, which meant that it was predicted that experiments would observe many types of magnetic behavior in this material.

Typically, the lattice structure of a crystallite of iron is body-centered cubic (bcc). This is the so-called α -phase of iron. In a bulk piece of iron, the fcc, or γ -phase, does not exist below 1200 K, a temperature which is far too high for magnetic ordering to occur [3]. Prior to the 1980s, fcc iron could only be produced at high temperatures, or as inclusions in a Cu matrix that were found to be anti-ferromagnetic [4]. Copper has an fcc atomic structure, and it was later found that the thermodynamically unstable γ -phase could be studied at room temperature in the form of ultrathin films on its surface.

By now, iron on the (100) surface of copper has become perhaps the most extensively studied magnetic ultrathin film system. This is partly because the system is one of a handful that exhibit a magnetic easy axis that is perpendicular to the film plane, which is of technological interest because, when used as recording media, one

can potentially achieve high densities of magnetic bits. More importantly, this system has an extremely complex and interesting magnetic phase diagram [5] (see Fig. 3.1) which means that it provides an instructive playground for learning about the interplay between structure and magnetism. At thicknesses below two monolayers (ML), no magnetic response is observed. Between two and four atomic layers, the films exhibit a perpendicular easy axis of magnetization and Kerr effect measurements show that the total moment increases linearly with thickness, which is expected for a uniformly magnetized film. The magnetic moment drops suddenly at ~ 4 ML, and remains constant until the thickness reaches ~ 11 ML, as shown in region II in the figure. This behavior has been found to be due to the fact that only the top two layers are ferromagnetic in this regime. The exact spin structure of the layers underneath has been the subject of a lengthy debate [7] which we will not concern ourselves with here, but it is agreed that they have no net moment. Finally, the magnetization falls to the in-plane direction when the film thickness reaches ~ 12 ML.

These three regimes of differing magnetic behavior can be associated with observed changes in the structure and growth mode of these films. Diffraction studies have shown that the decrease in perpendicular moment that occurs at 4 ML is tied to a structural transition in which all but the top two layers transform from a distorted face-centered cubic (fct, or face-centered tetragonal) phase to an undistorted fcc phase. The spin-flop transition at 12 ML is accompanied by a so-called “Martensitic” structural transition from fcc to bcc [8-11]. The growth of the film is also correlated with these changes in that layer-by-layer growth begins at ~ 4 ML and ends abruptly when the spin-flop and fcc-bcc structural transition occurs.

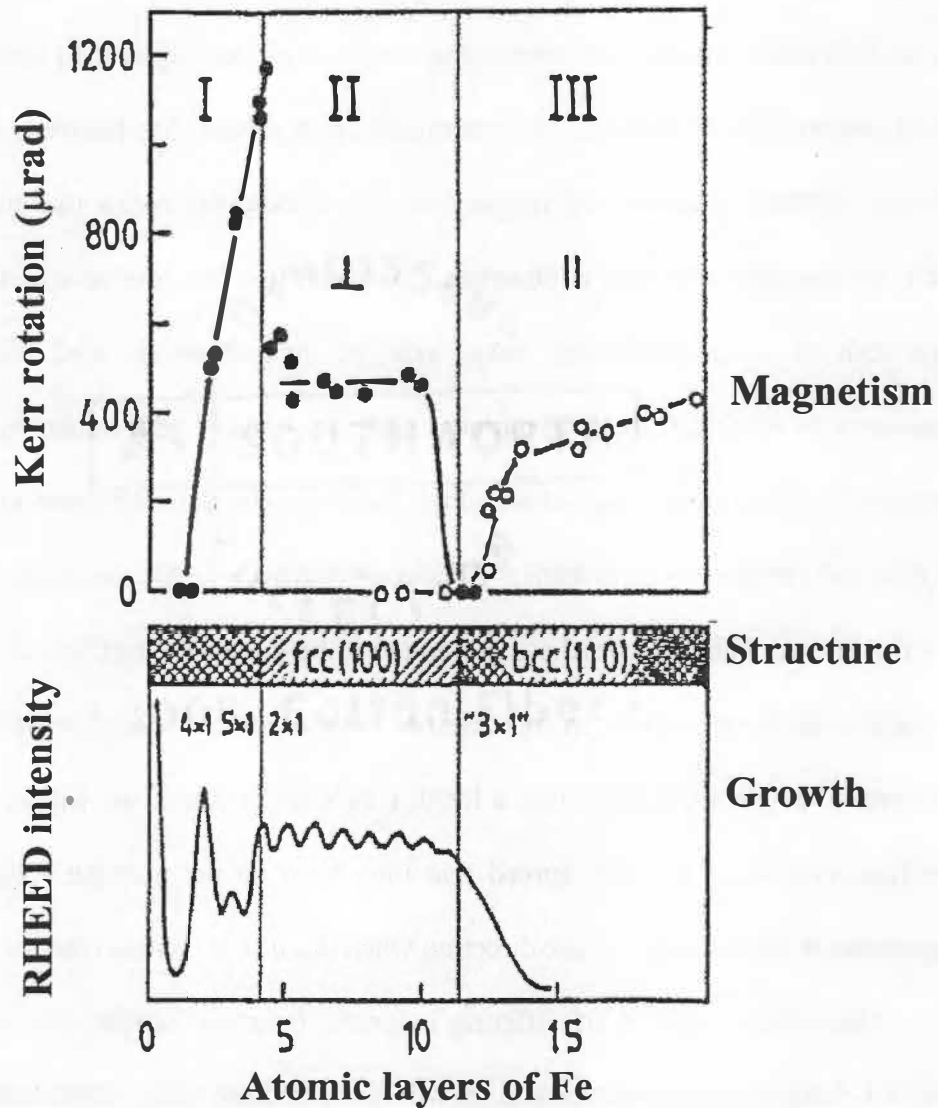


Figure 3.1: Magnetism, structure, and growth of Fe films on Cu(100) [from ref. 5]. The behavior of room-temperature-grown Fe/Cu(100) films is quite complex. Iron films that are 2-4 layers thick are ferromagnetic, of a distorted fcc structure, and do not grow in an ideal, layer-by-layer mode. In this regime they are magnetized perpendicular to the film plane. When the film thickness reaches ~ 4 atomic layers, the magnetic moment decreases suddenly, and remains constant with increasing thickness due to the fact that all but the top two layers have become undistorted fcc and are either anti-ferromagnetic or non-magnetic [6]. RHEED oscillations indicate excellent layer-by-layer growth. When the film thickness reaches 12 monolayers, a magnetization reorientation occurs that is associated with an fcc to bcc structural transition.

3.1.2 The problem of understanding magnetism in metastable films

As we discussed in chapter two, the direction of the easy axis of magnetization in a magnetic film is determined by a competition between anisotropy induced by the lattice structure of the film, which may favor perpendicular or in-plane magnetization, and shape anisotropy, which always favors in-plane magnetization and grows stronger as the film thickness is increased. Shape anisotropy guarantees that a film that shows perpendicular magnetization at low thickness will undergo a spin-flop transition and develop in-plane magnetization as its thickness is increased through some critical value. This was observed, for example, in Co films on the Au(111) surface [12]. In that case, the easy axis was found to reorient from the perpendicular to the in-plane direction at a film thickness of approximately 4.5 atomic layers. As Oepen *et al.* show in that work, simply observing the critical thickness for a thickness-driven spin-flop transition provides direct, quantitative information about the strength of the anisotropies in the system that makes it possible to evaluate its anisotropy constants.

This approach cannot be used to learn the contributions to the anisotropy in fct iron films on Cu(100). The root of the problem can be seen in the phase diagram in Fig. 3.1. A structural transition from fct to fcc precedes the spin reorientation transition, which means that we never get to see the competition between the in-plane shape anisotropy and perpendicular magnetocrystalline anisotropy "play out" in this system. The fact that, at a thickness of 4 ML, the system transforms to a configuration in which only the top two layers are ferromagnetic means that the shape

anisotropy energy ($2\pi M^2 d$) stops growing with thickness (d). This, in turn, means that the thickness for spin reorientation is *delayed* in the sense that it occurs at a higher thickness than it would have if the film remained uniformly magnetized. The matter is clouded further by the fact that when the film finally does undergo a spin-flop transition at 12 ML, it is associated with another structural transition. Indeed, for determining the contributions to the anisotropy in this system, it is useful to learn the *true* critical thickness for spin reorientation that we would observe in the *absence* of these structural changes.

Recent work on perpendicularly magnetized Fe/Cu(100) ultrathin films has provided further motivation for finding the true critical thickness of these films. Magnetic domain imaging has revealed interesting evolution in their magnetic domain structure as the film thickness is varied at a fixed temperature [13]. As seen in Fig. 3.2 and its caption, two-step disordering of a micrometer-sized stripe phase has been observed. Theoretically, the melting of these striped domains could result from the close proximity of the system temperature to either the critical temperature for a spin reorientation, or to the critical temperature for a ferromagnetic to paramagnetic phase transition (the Curie temperature), depending on which one is lower. This issue could, in principle, be resolved by obtaining a magnetic phase diagram for the system that shows the thickness and temperature dependence of the reorientation of its easy axis.

As can be seen at the top of Fig. 3.1, the phase diagram for this system, while extremely interesting, shows magnetic transitions that are greatly affected by various structural changes. The stripe phase melting, however, is likely to be a purely

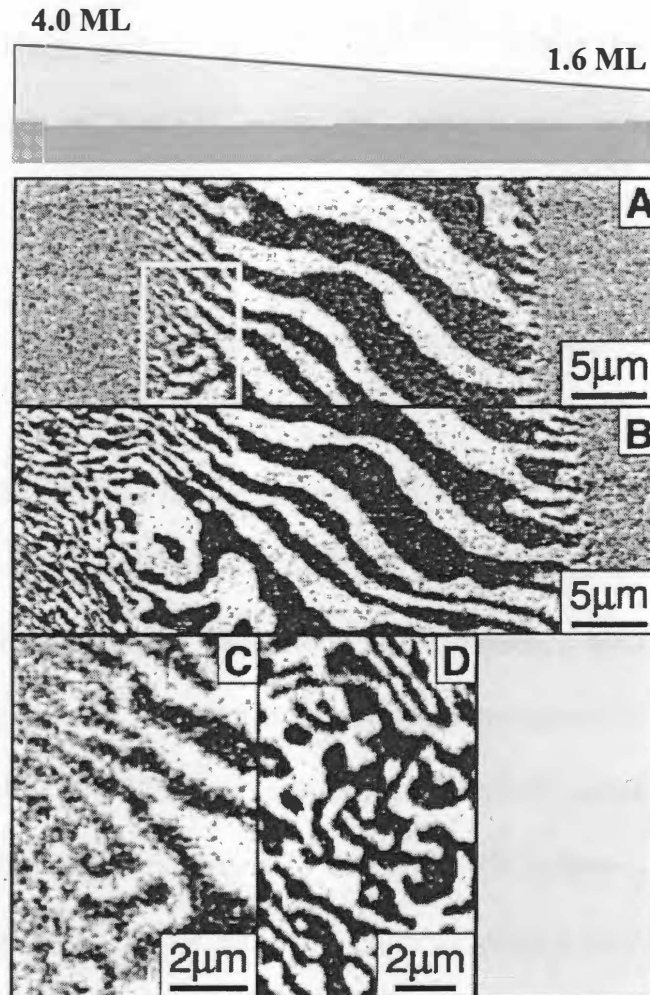


Figure 3.2: Two-step disordering of perpendicular magnetization in Fe/Cu(100) ultrathin films [adapted from ref. 13]. Images (a) and (b) are SEMPA images of perpendicular magnetic domains in a wedge-shaped iron film on Cu(100). Image (a) was recorded at room temperature and image (b) was recorded at 200 K. As the film thickness is increased, the magnetic domains lose their oriented-stripe order and then vanish completely. Images (c) and (d), respectively, are zoomed-in views of a transition regime in which orientational order is being lost and an area in which the domains have no orientational order. Obtaining a magnetic phase diagram for fct Fe/Cu(100) would tell us whether the disordering seen here is due to the approach of the system to its Curie temperature, or if it is associated with an imminent spin reorientation transition.

magnetic phenomenon since it was observed in the thickness (< 4 ML) and temperature (< 310 K) regime in which the films are structurally uniform and in the face-centered tetragonal phase. A thorough understanding of this stripe phase melting requires a *pure* magnetic phase diagram that describes the system in the absence of the structural transitions.

3.1.3 *Inducing spin reorientations with Co capping atoms*

Here, we employ a method involving magnetic capping atoms to obtain information about the magnetic phase diagram of the underlying Fe/Cu(100) films in the absence of structural transitions. It is known that magnetic capping atoms can modify the effective anisotropy of a system such that an SRT can take place when the number of capping atoms thickness reaches some critical value [14-16]. We have previously reported a method for using this phenomenon to determine the critical thickness of SRT for the uncapped Fe film [16]. Here, we use this technique to map a *pure* magnetic phase diagram that completely separates out the influence of structural transitions. The phase diagram indicates that the critical temperature for SRT of the Fe/Cu(100) system is in fact lower than the Curie temperature, which implies that the melting of the stripe phase reflects the proximity of the system to SRT temperature rather than the Curie temperature. Our data have also been used to determine the temperature dependent anisotropy constants for the Fe/Cu(100) films.

Experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure lower than 7×10^{-11} Torr. The system was equipped with facilities for

low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and magneto optic Kerr effect (MOKE) studies. It was possible to operate the MOKE setup in both polar and longitudinal geometries by rotating the magnet around the sample. The Cu substrate was prepared by cycles of sputtering with Ne ions and annealing to 900 K until clean AES spectra and sharp (1×1) LEED patterns were obtained.

The Fe and Co films were evaporated from Fe and Co wires heated by electron beam bombardment. The high-purity (99.995%) source wires were oriented so that they pointed toward the substrate and their tips were at the center of a hoop-shaped tungsten filament, as shown in the schematic in Fig. 3.3. Placing a positive bias of 800-900 V on the wire and running approximately 2 Amperes of current through the heater filament was typically sufficient to begin evaporating the source material. The rate at which the source material was evaporated was monitored with flux monitors that were mounted on each source. The flux monitors were nothing more than bare wires which collected a fraction of the ionized source atoms as they passed out the end of the doser. This generated a small (typically ~ 200 nA) current in the flux monitor wire, which could be measured. The stability of the evaporation process was established by controlling the current through the heater filament such that the flux current was constant.

The relationship between the flux monitor reading and the rate at which material was actually deposited on the substrate was established with scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). STM is the best technique for establishing the absolute coverage of ultrathin overlayers on

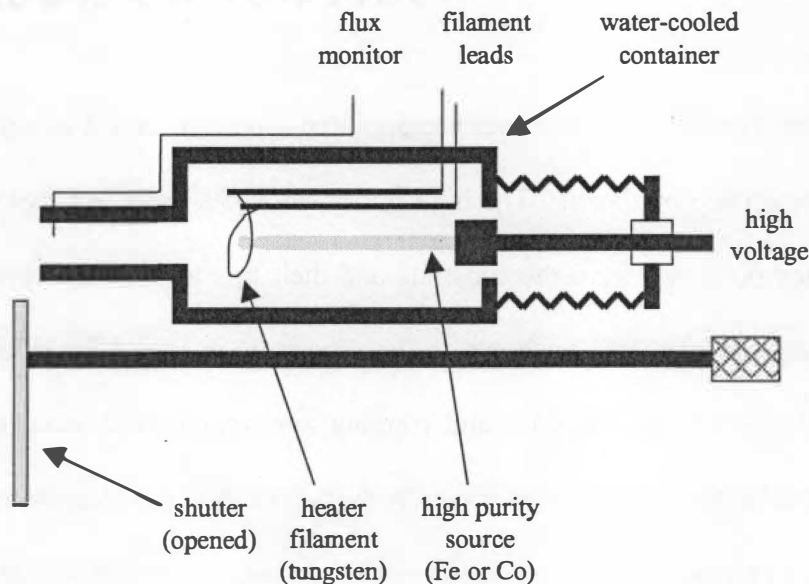


Figure 3.3: Anatomy of an evaporator for molecular beam epitaxy. A high-purity source is mounted so that it can be positioned at the center of a loop-shaped heater filament. A high, positive voltage is applied to the source so that electrons ejected from the heater filament via thermionic emission will be attracted to the source and help to heat it. Evaporated source atoms, which can be neutral or ionized, either coat the inner walls of the evaporator or travel out the open end (at left in the schematic). The metal can that contains the filament and source is water-cooled to help maintain the ultrahigh vacuum environment. If it weren't cooled, contaminants would come off of the walls of the apparatus as it was heated by the filament and source. The fraction of ionized atoms that contact the flux monitor wire are "counted" by measuring the current that they generate as they are neutralized by electrons in the flux monitor wire.

substrates. One typically generates a histogram of the heights that correspond to each pixel in the image. For instance, in the 1 ML Fe/Cu(111) film shown in Fig. 4.13 in the next chapter, 5% of the surface is exposed substrate, 95% of the surface is one atomic layer above the substrate, and 5% of the surface is occupied by a double-layer. STMs are becoming more and more prevalent, but are still expensive and can't yet be regarded as conventional equipment that can be found on any surface analysis system. For this reason, it is useful to use STM to establish the thickness dependence of signal that can be observed with another technique. For the case of Fe on the (100) and (111) surfaces of copper, STM has been used to establish the thickness dependence of the iron and cobalt peak intensities in Auger electron spectra.

In Auger electron spectroscopy, a beam of 3000 eV electrons is directed at a sample. Some of these electrons knock core electrons out of the atoms of the sample, leaving a vacancy in that electron level. As valence electrons fall from higher levels to fill the vacancy, they give up energy. This energy can be emitted as a photon or, alternatively, could be given to another electron, called an "Auger electron", that is ejected from the sample. The energy of the Auger electron depends only on the energy level spacings of the material from which it came, and not on the energy of the electrons in the incident beam. For this reason, a record of the energy of the Auger electrons provides a chemical fingerprint of the species present in the sample.

In performing Auger spectroscopy, one typically records the intensity (counts per second, or N) of the outgoing electrons as a function of their energy and then plots the first derivative of N with respect to energy versus the energy. Two of these spectra are shown in Fig. 3.4(a). The top spectrum was recorded from a copper

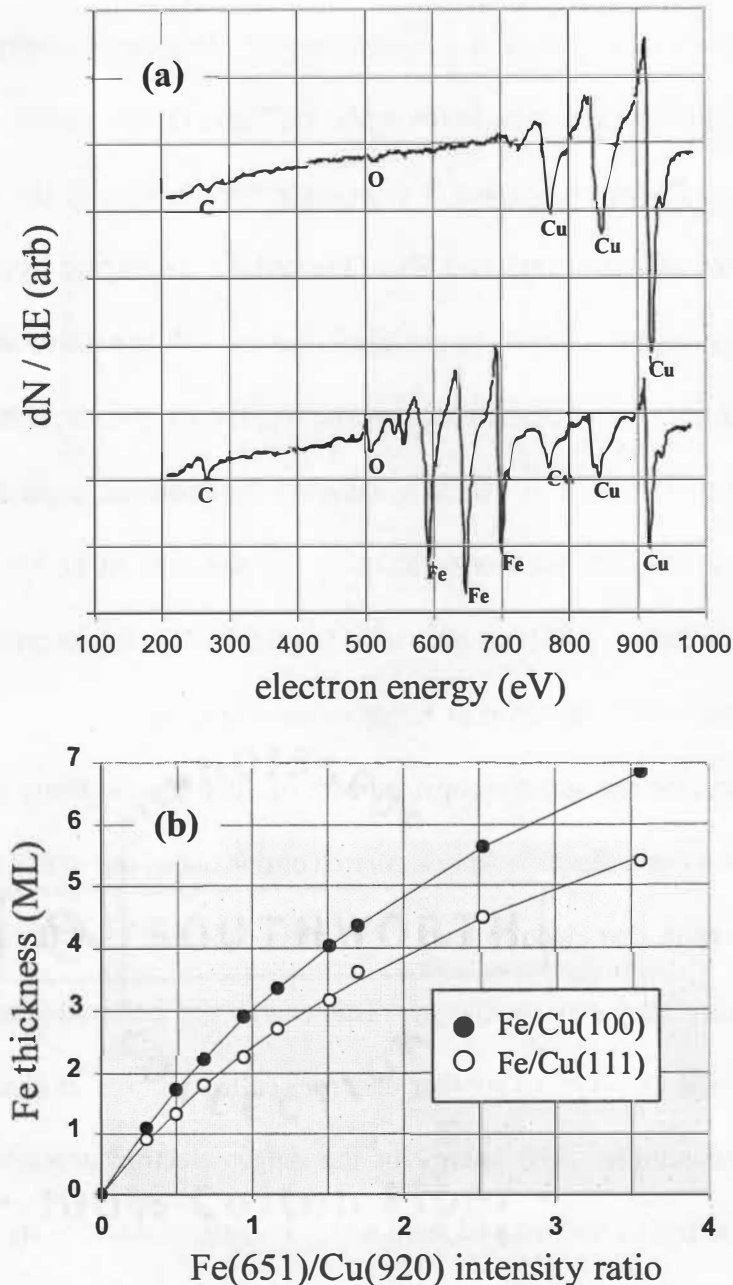


Figure 3.4: Using Auger spectroscopy to confirm cleanliness and calibrate film thickness. (a) Auger scans taken before (top) and after (bottom) deposition of Fe on a copper surface. In this case, the presence of C and O indicates that the Fe source is not yet clean. (b) Calibration curve established with STM for using Auger peak ratios to determine thickness. Iron does not grow as smoothly on the Cu(111) surface (see Fig. 1 in Chapter 4), and the resulting holes in the Fe(111) films make it easier for Auger electrons to escape from the underlying Cu substrate. This is one reason for the difference in the calibration curves for the two surfaces. In the Auger scan in (a) of the Fe covered substrate, the ratio of the heights of the Fe and Cu peaks is 1.317. This corresponds to a thickness of 3.67 atomic layers.

substrate. The bottom spectrum was recorded from the same substrate after 3.67 atomic layers of Fe were deposited on its surface. The lineshapes and peak positions in these spectra correspond extremely well to those shown in standard spectra for Fe and Cu. As one deposits Fe on a clean Cu substrate, the peaks corresponding to the Fe Auger transitions grow and the Cu peaks shrink. This is because Auger processes become more and more likely to occur in Fe atoms as more are added to the sample. As the Cu substrate is buried by the Fe overlayer, Auger electrons from the Cu become less likely to escape the sample without undergoing a scattering process that changes their energy. These effects lead to extreme surface sensitivity, which can be seen in the figure in the fact that with only 3.67 layers of Fe on the surface, the Fe peaks are larger than those originating from the copper underneath.

By recording Auger spectra and STM images at various doseages, it was possible to generate the buildup curves shown in Fig. 3.4(b), which relate the height ratio (R_{Fe-Cu}) of the largest Fe and Cu peaks to the absolute Fe coverage. The curves for Fe on the (100) and (111) surfaces are fit by the functions $5 \ln(1 + 0.822 R_{Fe-Cu})$ and $4 \ln(1 + 0.822 R_{Fe-Cu})$ respectively. A similar study has been performed for Co on the Cu(100) surface, which can be fit by $5 \ln(1 + 0.750 R_{Co-Cu})$. The *ratios* of these peaks are used instead of the absolute heights of the Fe or Co peaks alone because this normalization compensates for irregularities in the sample position and/or the Auger electron gun intensity.

The iron films that we studied were always less than 4 ML thick and were grown at room temperature (RT) to insure that they were of the fct structure. After the growth of the Fe films, Co capping atoms were subsequently deposited onto the Fe

film at 110 K. The STM morphology of this system is shown in Fig. 3.5. The capping atoms were added in steps as small as 0.005 monolayers and polar and longitudinal MOKE measurements were made after each deposition.

SMOKE hysteresis loops are shown for a 3.8 ML Fe film as a function of Co-capping atom coverage in Fig. 3.6. The loops in the left column correspond to the behavior of the system as an applied magnetic field is swept between plus and minus 400 Oe along the direction normal to the surface (polar Kerr effect). In this geometry, the observed SMOKE signal is proportional to the component of the sample magnetization that is along the surface normal. The equivalence of the remanence, or zero-field magnetization to the saturation magnetization in the loops at the upper left of the figure shown that the magnetization of the system is quite content to point along this direction. As Co is added in steps of 0.02 ML, the polar Kerr loops gradually change their shape. They indicate that it becomes harder to force the moments to point along the surface normal as Co is added.

The loops in the right column of Fig. 3.6 were recorded in the longitudinal geometry, in which the magnetic field is applied in the plane of the sample. At a Co overlayer thickness of 0.08 ML, a faint amount of longitudinal Kerr response becomes observable. When the Co coverage is increased further, the evolution of the in-plane magnetization curves indicates that a spin-flop transition has occurred. The preferred orientation of the magnetization of the system has changed from the perpendicular to the in-plane direction.

Figure 3.7 demonstrates another spin reorientation as observed in a 2.65 ML Fe film induced by Co capping layers at 105 K. The ratios of remanent (M_r) to

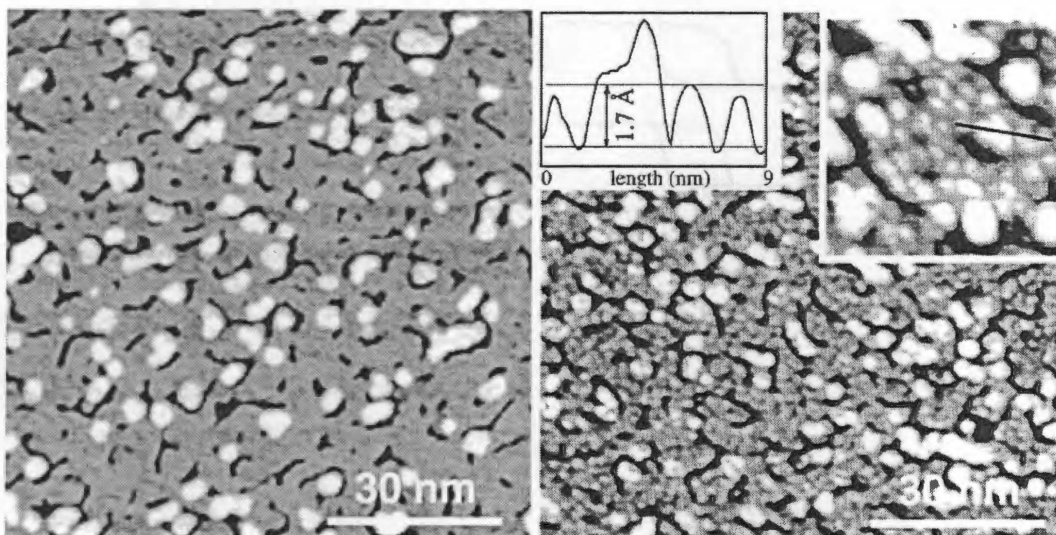


Figure 3.5: STM morphology of a 3.1 ML Fe/Cu(100) film before (left) and after (right) capping with 0.5 ML Co. Both images were recorded at 110 K. The inset in the upper right corner of the image of the cobalt-capped film shows a $20 \times 20 \text{ nm}^2$ area. The height profile along the dark line in the inset is shown in the upper left corner. It indicates that the small islands, which are likely to be cobalt, are one atomic layer high.

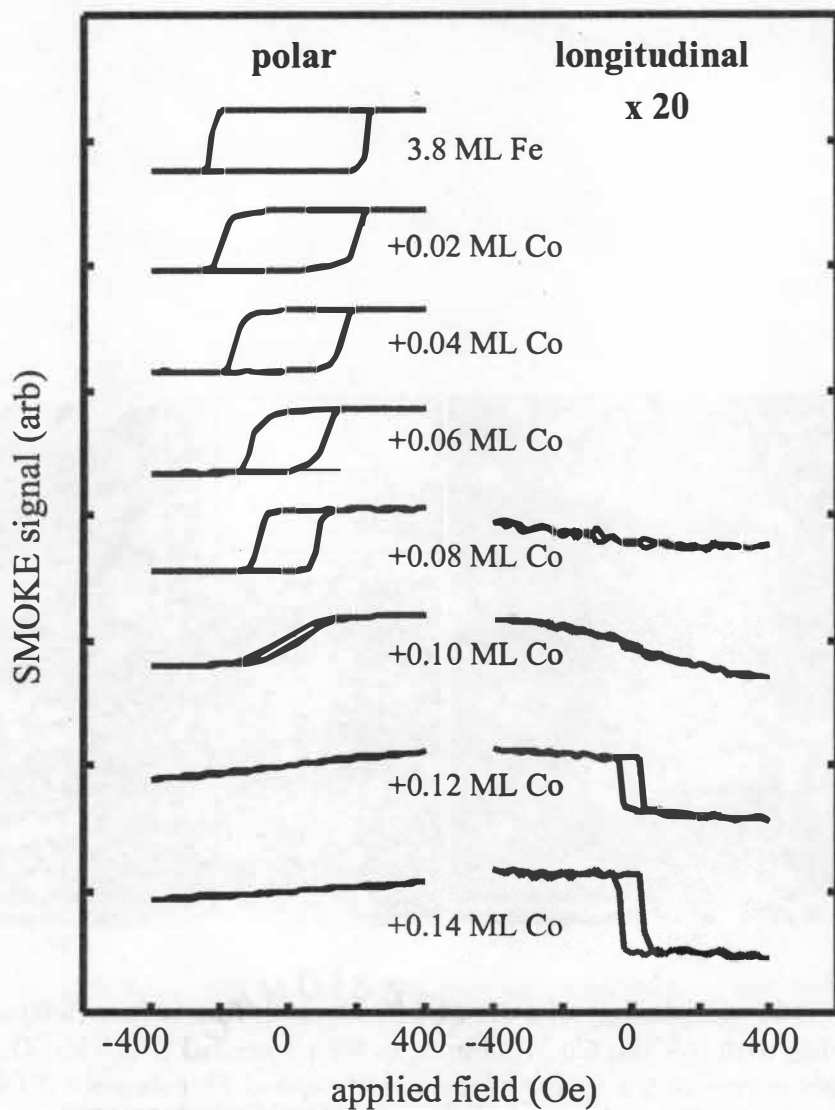


Figure 3.6: SMOKE hysteresis loops of a Co capped Fe/Cu(100) film. As cobalt is added in doses of 0.02 atomic layers, the easy axis of magnetization begins to reorient from the perpendicular to the in-plane direction, as evidenced by the disappearance of polar hysteresis and the appearance of longitudinal (in-plane) hysteresis.

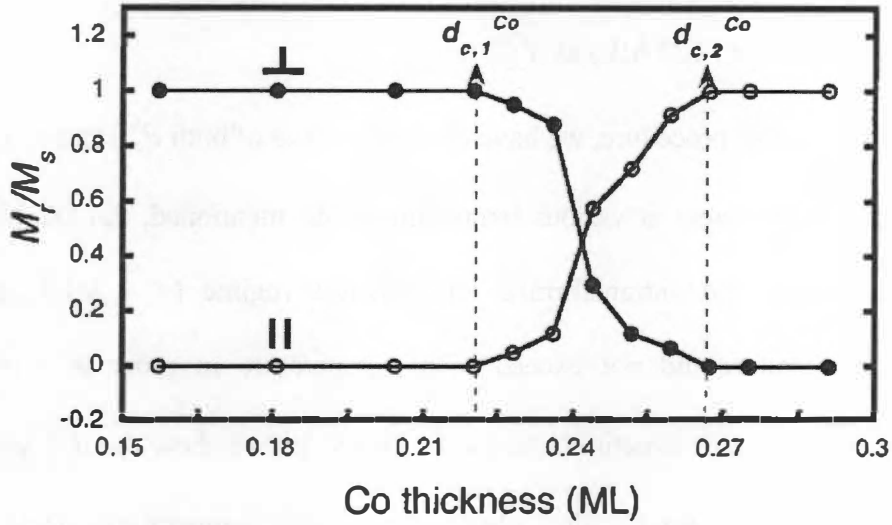


Figure 3.7: Spin-flop transition in a Co capped 2.65 ML Fe/Cu(100) film. The plot shows the ratio of the remanent magnetization (M_r) to saturation magnetization (M_s) for this sample with the magnetic field applied along the perpendicular (filled circles) and in-plane (open circles) directions as a function of Co capping layer thickness. The measuring temperature was 105 K. It is clear from the disappearance of the perpendicular signal and the appearance of in-plane magnetization that the capping layer has induced a spin reorientation in the underlying Fe film. The values $d_{c,1}^{Co}$ and $d_{c,2}^{Co}$ denote respectively the cobalt thickness at the onset and completion of the transition.

saturation (M_s) magnetization as determined from both polar (filled circles) and in-plane (open circles) MOKE hysteresis curves are displayed as a function of the amount of Co adatoms. A perpendicular to in-plane SRT clearly starts to take place at about 0.22 ML of Co thickness, as evidenced by the decrease of perpendicular M_r and the increase of in-plane M_r . When the Co thickness amounts to 0.27 ML, the in-plane M_r reaches saturation and the perpendicular M_r decreases to zero, indicating the completion of the SRT. We denote the starting point of the SRT (0.22 ML) as $d_{c,1}^{Co}$, and the finishing point (0.27 ML) as $d_{c,2}^{Co}$.

Following this procedure, we have obtained values of both $d_{c,1}^{Co}$ and $d_{c,2}^{Co}$ for Fe films of various thickness at various temperatures. As mentioned, the Fe thickness was limited within the untransformed fct thickness regime (< 4 ML), and the maximum temperature did not exceed room temperature in order to avoid any possible interdiffusion or structural change. In Figure 3.8 we show the $d_{c,1}^{Co}$ values as a function of thickness for Fe films obtained at various temperatures. Data points taken at each temperature clearly follow a linear fit, as indicated by the regression lines in the plot. The x -axis intercept of each isotherm gives the value of the starting thickness ($d_{c,1}^{Fe}$) at which an fct Fe/Cu(100) film would undergo a spin reorientation *without Co capping* at that particular temperature. For example, the easy axis of magnetization of a clean fct Fe/Cu(100) film at 210 K would begin to reorient from perpendicular to in-plane at a thickness of 4.4 ML if the previously mentioned fct $\rightarrow$ fcc structural transformation did not occur. The finishing point of the SRT of the Fe

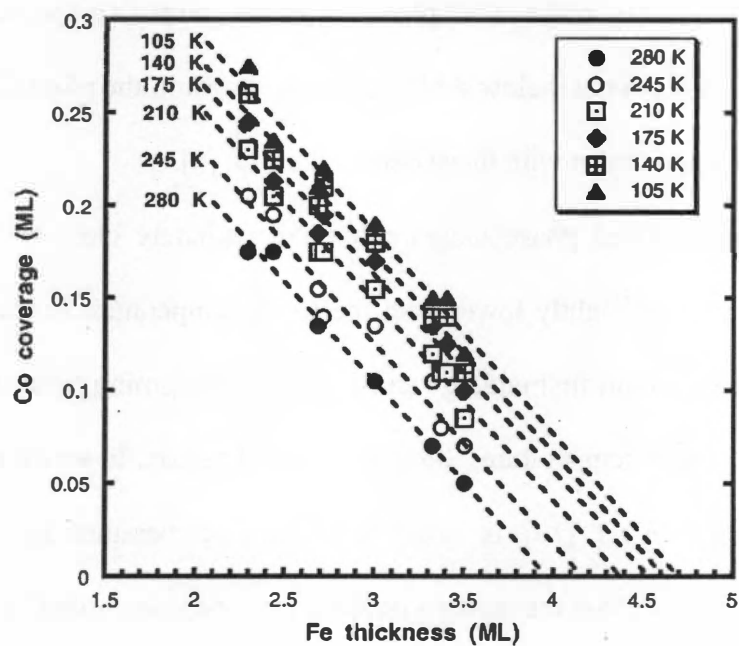


Figure 3.8: Isothermal plots of the capping layer thickness required to start the spin reorientation as a function of base film thickness. Each set of data can be fit with a line that can be extrapolated to the axis that represents the absence of cobalt capping atoms. This extrapolation gives the thickness at which a *clean* fct Fe film would reorient at each temperature.

films ($d_{c,2}^{Fe}$) has been determined in a similar manner from the $d_{c,2}^{Co}$ vs. Fe thickness plot.

This data directly results in a magnetic phase diagram for fct Fe, as shown in Fig. 3.9. The shaded area represents the transition regime over which the easy axis of the film reorients from the surface normal to the in-plane direction. The left and right boundaries of the transition regime define the onset and completion of the SRT of Fe films, respectively. To make the phase diagram more complete, the Curie temperatures of the Fe films (below 4 ML) are also shown in the plot (filled squares), which are in good agreement with those obtained in ref. [6].

From the obtained phase diagram it is immediately clear that the critical temperature of SRT is slightly lower than the Curie temperature in the Fe/Cu(100) system. The system would first undergo an SRT before becoming paramagnetic when increasing thickness or temperature. Since the marked region, in which the stripeless phase was observed in ref. [13], is closer to the SRT temperature than to the Curie temperature, we believe that the melting of the stripe phase is caused by the onset of an SRT rather than by paramagnetism. This is not surprising since the system no longer has enough perpendicular anisotropy to sustain the up-down stripe domains when approaching the SRT. A similar breakdown of perpendicular domains has been observed in the low temperature grown Fe/Cu(100) system [17].

It is interesting that a temperature-driven SRT has never been reported for the RT grown Fe films, although the observation is difficult in practice because the SRT temperature is very close to the structural relaxation temperature (~ 310 K) [18].

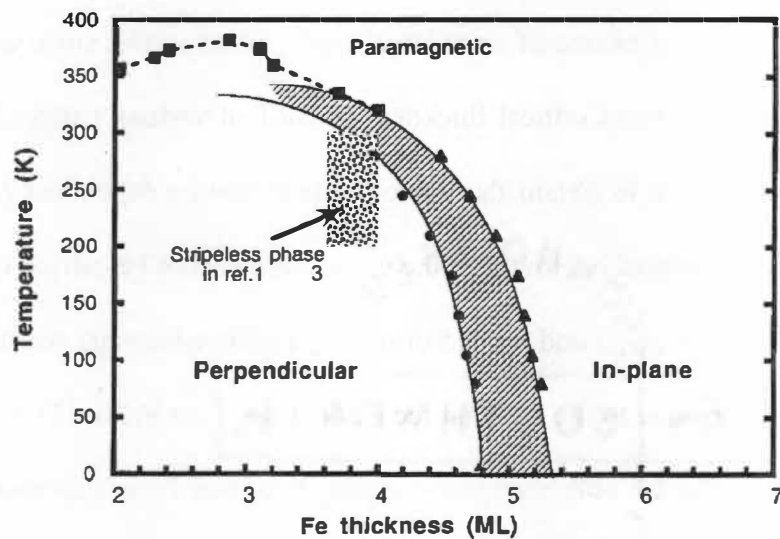


Figure 3.9: Magnetic phase diagram for fct Fe on Cu(100). The arch-shaped shaded area is a transition regime in which the magnetization is either canted or made up of perpendicular and in-plane domains. The boundary between the ferromagnetic, in-plane magnetized region and the paramagnetic region remains unknown because the Curie temperature for fct Fe films that are thicker than 4 ML cannot be observed due to the structural transition that occurs at that thickness.

3.1.4 Determining contributions to the anisotropy in fct Fe/Cu(100) films

The magnetic phase diagram can be used to calculate the temperature dependent anisotropy constants of the Fe films. Recently Millev, Oepen and Kirschner et al., by following the flowing trajectory in anisotropy space, were able to deduce both first (K_{1s}) and second-order (K_{2s}) surface anisotropy constants with [19] or without [12,20] the presence of an external field. In principle, since we have the data of the first and second critical thickness of SRT at various temperatures (Fig. 3.9), we should be able to obtain the values of temperature-dependent K_{1s} and K_{2s} following the same approach. However, the calculation cannot be carried out without the knowledge of first- (K_{1b}) and second-order (K_{2b}) bulk anisotropy constants of fcc Fe, which are lacking due to the fact that fcc Fe does not exist bellow 1150 K in bulk. It is not proper to use the bulk anisotropy constants of bcc Fe in this case, not only because bcc Fe has a different crystal structure, but also because the Fe/Cu(100) films have a greatly distorted fcc structure, which in turn should lead to considerably larger bulk anisotropy constants than those of undistorted bcc Fe.

For the reasons described above, we decide to concentrate only on obtaining first-order anisotropy constants for both surface and bulk. This, in fact, is nontrivial since the spin phase diagram alone does not provide enough information to deduce both the surface and bulk anisotropy constants of Fe/Cu(100) films. We therefore designed an experiment by using Fe capping layers to introduce a reversed SRT in a Co/Fe bilayer on Cu(100), as shown in Fig. 3.10. In the experimental procedure, a 1.2ML Co/1.2ML Fe bilayer structure was first grown on top of Cu(100) at room

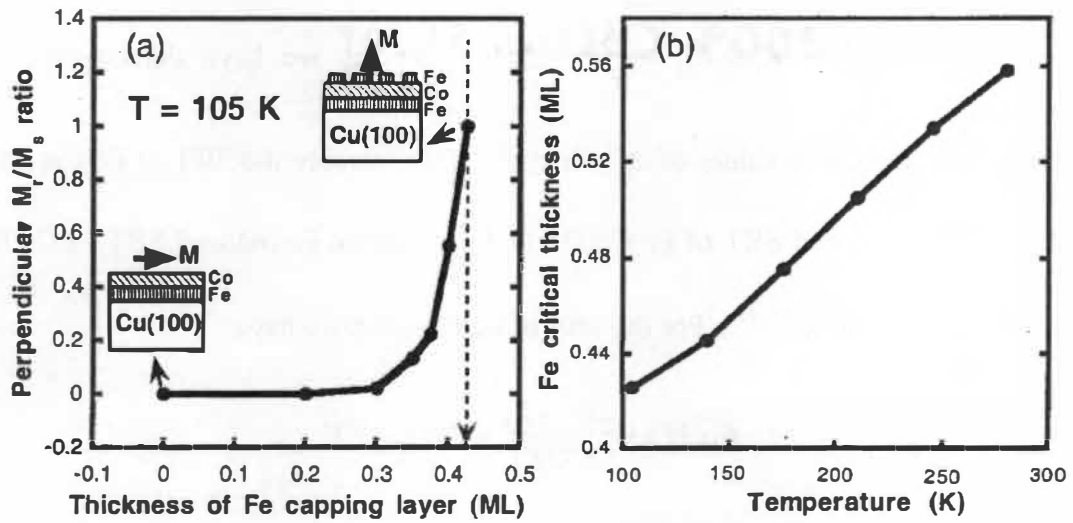


Figure 3.10: Reverse spin reorientation in a 1.2 ML Co/1.2 ML bilayer on Cu(100) induced by Fe capping atoms. (a) At 105 K, 0.43 atomic layers of Fe (indicted by the dashed arrow) are required to complete the in-plane to perpendicular spin flop. (b) The critical thickness of the Fe capping layer that is required to induce the transition was found at various temperatures.

temperature. Such a bilayer structure has an in-plane easy magnetization axis. Additional Fe atoms were then deposited on the Co/Fe bilayer at 105 K till the film became fully perpendicular magnetized (marked by the arrow with dashed line in Fig. 10(a)). The amount of Fe needed to complete this reversed SRT is denoted as $d_{c,2}^{Co/Fe}$, the temperature dependence of which is shown in Fig. 3.10(b). Based on the argument made in refs. [12] and [20], the first-order crystalline anisotropy (including both surface and bulk) cancels out with shape anisotropy at the thickness where SRT has been completed, i.e. $K_1 = K_{1b} + \frac{2K_{1s}}{d_{c,2}} = 2\pi M^2$. So far we have determined the temperature-dependent values of $d_{c,2}$ for three SRTs, namely the SRT of Fe/Cu(100) ($d_{c,2}^{Fe}$), the Co induced SRT of Fe/Cu(100) ($d_{c,2}^{Co}$), and the Fe induced SRT of Co/Fe bilayer on Cu(100) ($d_{c,2}^{Co/Fe}$). For the SRT of Fe/Cu(100), we have

$$K_{1b}^{Fe}(T) + \frac{2K_{1s}^{Fe}(T)}{d_{c,2}^{Fe}(T)} = 2\pi M_{Fe}(T)^2$$

For the Co-induced SRT of Fe/Cu(100), we have

$$\begin{aligned} & \left(\frac{K_{1b}^{Fe}(T)d_{c,2}^{Fe} + K_{1b}^{Co}(T)d_{c,2}^{Co}(T)}{d_{c,2}^{Fe} + d_{c,2}^{Co}(T)} \right) + \frac{[(2 - \varphi(T))K_{1s}^{Fe}(T) + \varphi(T)(K_{1s}^{Co}(T) + K_{1s}^{Co-Fe}(T))]}{(d_{c,2}^{Fe} + d_{c,2}^{Co}(T))} \\ & = 2\pi \left(\frac{M_{Fe}(T)d_{c,2}^{Fe} + M_{Co}(T)d_{c,2}^{Co}(T)}{d_{c,2}^{Fe} + d_{c,2}^{Co}(T)} \right)^2 \end{aligned}$$

where $d_{c,2}^{Fe}$ is the thickness of the Fe base film, and $\varphi(T)$ is the coverage of the Co capping layer at the critical thickness of the SRT, which is the same as $d_{c,2}^{Co}(T)$ when it is expressed in units of monolayers. The equation above may appear hopelessly

complex, but its form is explained in full detail in section 2.2.3. The first term is essentially a weighted average of the bulk anisotropy energies of the two magnetic constituents in the system. The second term and the term to the right of the equal sign are weighted averages of the surface and shape anisotropies, respectively.

For the Fe induced SRT of Co/Fe bilayer on Cu(100), we have

$$\begin{aligned} & \frac{K_{1b}^{Fe}(T)(d_{Fe}^* + d_{c,2}^{Co/Fe}(T)) + K_{1b}^{Co}(T)d_{Co}^*}{d_{Fe}^* + d_{c,2}^{Co/Fe}(T) + d_{Co}^*} + \frac{(1 + \varepsilon(T))(K_{1s}^{Fe}(T) + K_{1s}^{Co-Fe}(T)) + (1 - \varepsilon(T))K_{1s}^{Co}(T)}{d_{Fe}^* + d_{c,2}^{Co/Fe}(T) + d_{Co}^*} \\ & = 2\pi \left(\frac{M_{Fe}(T)(d_{Fe}^* + d_{c,2}^{Co/Fe}(T)) + M_{Co}(T)d_{Co}^*}{d_{Fe}^* + d_{c,2}^{Co/Fe}(T) + d_{Co}^*} \right)^2 \end{aligned}$$

where d_{Fe}^* and d_{Co}^* are the thickness of Fe and Co in the Fe/Co bi-layer, respectively, and $\varepsilon(T)$ is equal to $d_{c,2}^{Co/Fe}$, the Fe thickness needed to complete the reverse spin-flop transition, in units of monolayers.

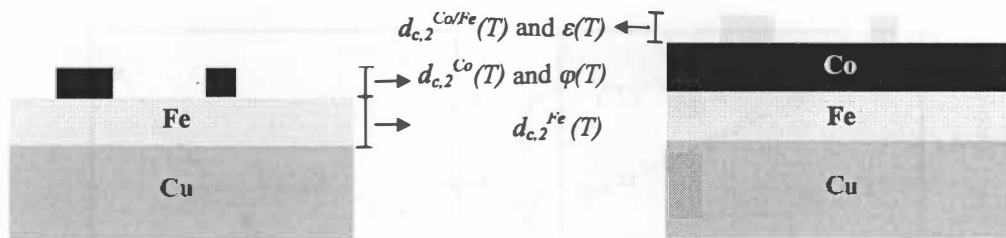
The first-order bulk ($K_{1b}^{Co}(T)$) and surface ($K_{1s}^{Co}(T)$) anisotropy constants of fcc Co(100) have been determined by Kowalewski *et al.* using ferromagnetic resonance (FMR) measurements on ultrathin films of Co/Cu(100) [21]. Although anisotropy constants were measured at only two temperatures (77 K and 295 K), it is reasonable to assume a linear temperature dependence and get anisotropy constants at other temperatures. By further taking bulk values of the magnetization of Fe ($M_{Fe}(T)$) and Co ($M_{Co}(T)$), we have three unknowns, i.e. $K_{1b}^{Fe}(T)$, $K_{1s}^{Fe}(T)$ and $K_{1s}^{Co-Fe}(T)$, left in equations (1), (2) and (3). For the convenience of readers, the known values of $d_{c,2}^{Fe}(T)$, $d_{c,2}^{Co}(T)$, $d_{c,2}^{Co/Fe}$, $K_{1b}^{Co}(T)$, $K_{1s}^{Co}(T)$, $\varphi(T)$, and $\varepsilon(T)$ at

various temperatures are summarized in Fig. 3.11. After some calculations, we have obtained values of $K_{1b}^{Fe}(T)$, $K_{1s}^{Fe}(T)$ and $K_{1s}^{Co-Fe}(T)$ as a function of temperature, as shown in Fig. 3.12. From Fig. 3.12 it is obvious that all these contributions to the anisotropy are positive (favoring perpendicular magnetization) and have a linear temperature dependence. The values of $K_{1s}^{Fe}(T)$ and $K_{1s}^{Co-Fe}(T)$, as expected, decrease with increasing temperature. It is somewhat surprising that $K_{1b}^{Fe}(T)$ increases with increasing temperature. In light of the possibility that $K_{1b}^{Fe}(T)$ most likely originates from strain-induced anisotropy, the increase of $K_{1b}^{Fe}(T)$ might be caused by an increase in film strain due to the different thermal expansion coefficients of fct Fe and fcc Cu. Similar behavior was also observed for Co ultrathin films on Cu(100).

In summary, we have demonstrated that magnetic capping layers can be used to generate a magnetic phase diagram for metastable magnetic Fe/Cu(100) ultrathin films. The magnetic phase diagram uncovers important information about the phase transitions of the Fe/Cu(100) system. In addition, we have shown that the anisotropy constants of Fe films display a linear temperature dependence. We believe that this method can be generalized to other metastable magnetic thin film systems.

3.1.5 *A new mechanism for inducing spin-flop transitions*

The magnetization direction of a magnetic ultrathin film is often determined by the magnetic surface anisotropy. Modifying this anisotropy by depositing a thin



Temperature (K)	$d_{c,2}^{Fe}(T)$ (10^{-8} cm)	$d_{c,2}^{Co}(T)$ (10^{-8} cm)	$d_{c,2}^{Co/Fe}(T)$ (10^{-8} cm)	$\phi(T)$	$\epsilon(T)$	$K_{1b}^{Co}(T)$ (10^6 erg/cm ³)	$K_{1s}^{Co}(T)$ (erg/cm ²)
105	9.31	0.69	0.77	0.41	0.43	-9.78	-0.478
140	9.20	0.67	0.80	0.39	0.44	-9.97	-0.437
175	9.11	0.64	0.86	0.38	0.48	-10.16	-0.399
210	8.80	0.62	0.91	0.36	0.51	-10.34	-0.360
245	8.44	0.58	0.96	0.34	0.53	-10.53	-0.320
280	8.05	0.55	1.00	0.32	0.56	-10.72	-0.281

Figure 3.11: Values used in calculating the contributions to the anisotropy in the Co-capped Fe/Cu(100) system. The temperature-dependent values of K_{1b}^{Co} and K_{1s}^{Co} are interpolated from ref. [19].

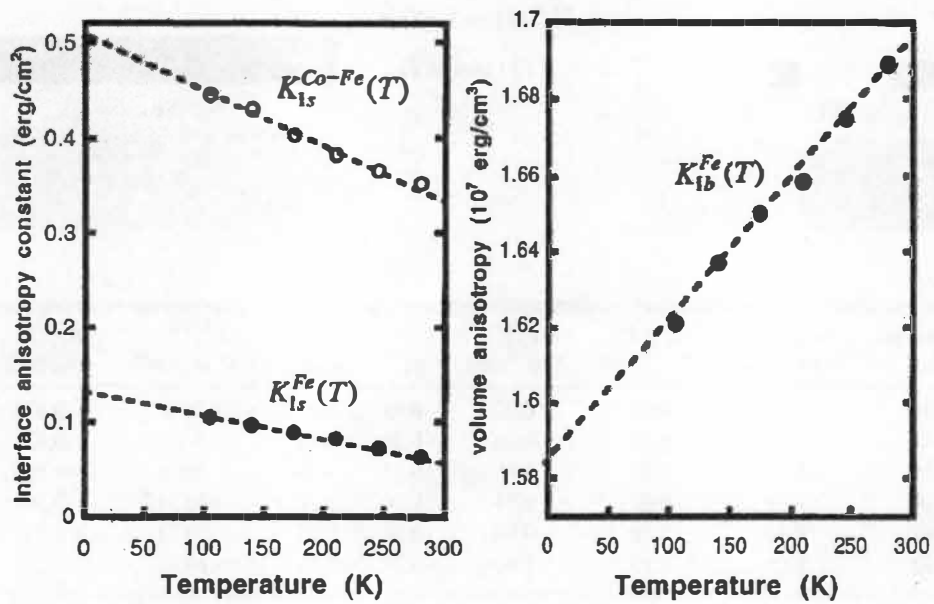


Figure 3.12: Temperature-dependent anisotropy constants for the cobalt-capped Fe/Cu(100) system. All anisotropy constants display a linear dependence on the temperature. The dashed lines are present to guide the eye.

capping layer or adsorbing gas molecules can result in a 90 degree rotation of the magnetization direction which is called a spin reorientation transition (SRT). Typically, the amount of deposited or adsorbed material plays the most crucial role in determining the onset of these transitions [15-16, 22]. On vicinal, or miscut surfaces, which have a larger number of step edge sites than flat surfaces, it has recently been shown that the spatial arrangement of deposited material on the surface can also contribute to a SRT [23-24]. The broken symmetry of the electronic environment at the step edge sites can lead to an additional uniaxial anisotropy. For this reason, preferentially depositing atoms along these step edges can drastically modify the magnetic anisotropy of the system. These modifications can be dramatic, as observed in stepped Co/Cu(100) ultrathin films, which undergo a SRT after a tiny number of Cu atoms are introduced at the step edges [24].

While this effect is intuitive on surfaces with parallel arrays of step edges, the effect of the arrangement of adatoms on the magnetic anisotropy of flat surfaces is far less obvious. In this work, we present experimental and theoretical evidence that indicates that modifying the spatial arrangement of cobalt capping atoms can drive a SRT in ultrathin Fe films grown on *flat* Cu(100) surfaces. As we will show, changes in the spatial distribution of a fixed quantity (0.18 monolayers) of cobalt capping atoms appear to be responsible for driving a perpendicular to in-plane rotation of the magnetization direction of a 2.8 monolayer (ML) Fe/Cu(100) film. The magnetization of this system then rotates back to the perpendicular direction when the Co and Fe atoms are intermixed at the surface. These observations support the results of our *ab-initio* calculations that predict that increasing the uniformity of the Co adatom

distribution or producing a FeCo alloy layer at the surface tends to increase the perpendicular anisotropy of the system.

Experiments were performed in an ultrahigh vacuum system with a base pressure lower than 7×10^{-11} Torr. The Fe films were grown by e-beam evaporation from an Fe wire (5N purity) onto a single crystal copper (100) surface at room temperature. Prior to Fe deposition, the Cu substrate was prepared by cycles of sputtering with neon ions and annealing to 900 K until clean Auger electron spectroscopy (AES) spectra and sharp (1×1) low energy electron diffraction patterns were obtained. STM studies indicated that the Cu surface was atomically flat with an average terrace width on the order of 200 nm. Cobalt atoms were subsequently deposited onto the Fe film at 110 K. As we showed earlier, the addition of Co atoms eventually causes a rotation of the easy axis of magnetization of the system from the perpendicular to the in-plane direction. Cobalt was added to the surface of the Fe film in small steps until we were able to observe magneto optical Kerr effect (MOKE) hysteresis loops in both the perpendicular and in-plane directions, which indicated that the Fe film was in a transition regime between the two orientations. The Co capped Fe/Cu(100) film was then briefly annealed to a given temperature for 10 seconds and cooled to 110 K for MOKE measurements.

Magnetic measurements of these Co capped Fe/Cu(100) films indicate that annealing the system leads to two SRTs. The first SRT, from perpendicular to in-plane, occurs after the film is annealed to temperatures between 110 K and 150 K. Figure 3.13 shows the combined results of two experiments. The results of the first experiment are shown in the figure at temperatures below 160 K. The M_r/M_s

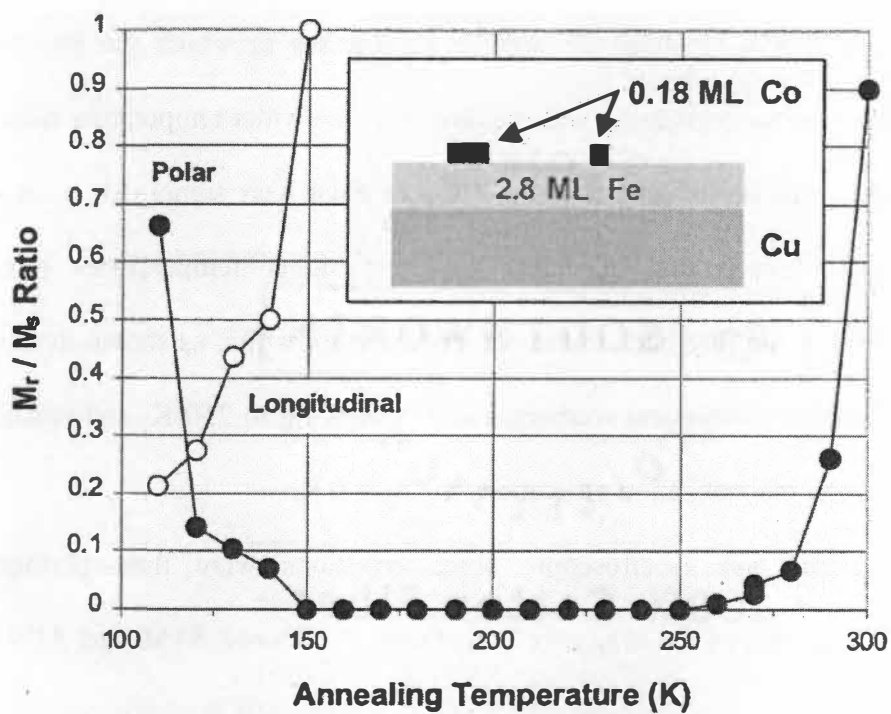


Figure 3.13: An unexpected series of spin-flop transitions. The plot shows the ratio of remanent to saturation magnetization, as observed in SMOKE hysteresis loops acquired at 110 K, versus annealing temperature. The easy axis completes a perpendicular-to-in-plane rotation after the sample is annealed to 150 K and begins to return to the perpendicular direction after annealing to 250 K.

(remanent to saturation magnetization) ratios of both in-plane and perpendicular magnetization curves, as measured at a fixed temperature of 110 K, are given. The temperature axis in the plot indicates the temperature to which the sample was annealed prior to the measurements. After annealing to 150 K for 10 seconds, the perpendicular component vanishes and the film becomes fully in-plane magnetized. The data shown in the figure at 160 K and above are the results of another experiment on a film of nearly identical Co and Fe thicknesses in which the perpendicular component of the magnetization was monitored over a wider temperature range. This second experiment reproduced the initial loss of polar Kerr signal that occurs below 140 K, and showed that annealing to even higher temperatures brings the magnetization of the film back to the perpendicular direction, as shown in the figure. The perpendicular component reemerges after annealing to 250 K, and reaches 90% of the saturation magnetization after annealing to 300 K.

Structural and spectroscopic characterizations were then performed to determine the origin of the magnetic transitions. Combined STM and AES studies reveal that annealing the Co capped Fe/Cu(100) film results in a redistribution of Co adatoms on the Fe surface. As shown in Fig. 3.14, the as-grown Co atoms form monolayer high clusters (~ 1 nm in diameter) that are distributed on the Fe surface with no apparent spatial order. After annealing to room temperature, the Co clusters coalesce into 2D islands with a typical size of 5-10 nm. Figure 3.15 illustrates the changes that were observed in the Auger spectrum of a 2.5 ML Fe/Cu(100) film capped by 1.0 ML of Co as the annealing temperature was increased. At temperatures below 140 K, there is no significant change in the Fe(47) and Co(53)

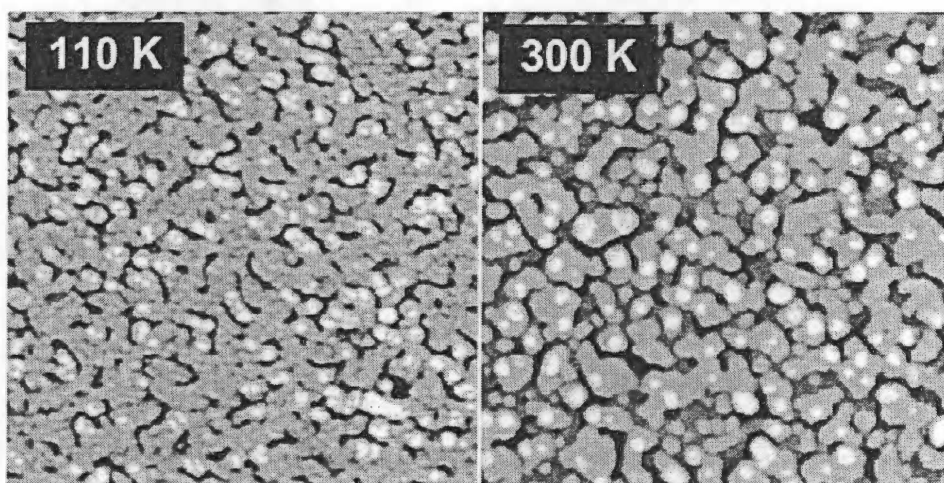


Figure 3.14: STM surface morphology of 0.5 ML Co on 3.1 ML Fe/Cu(100). The area shown in each image is $90 \times 90 \text{ nm}^2$. Three different atomic layers are visible in the both images (black, grey, and white). The roughness of the grey layer in the 100 K image was not present before Co deposition and indicates the presence of tiny Co islands. The images indicate that the Co islands become more mobile and merge, forming larger islands as the system is annealed.

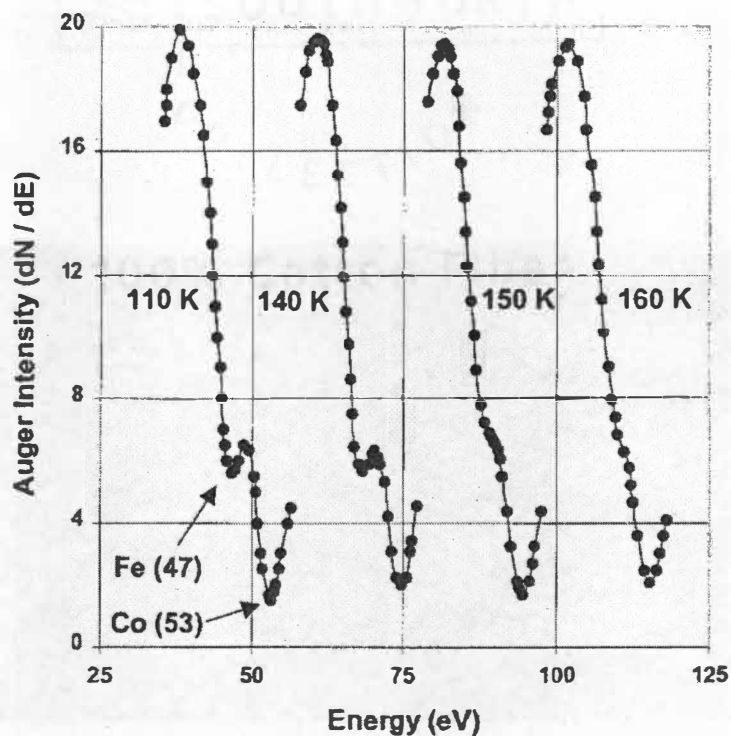


Figure 3.15: Annealing temperature dependence of Auger spectra acquired from a 2.5 ML Fe film capped with 1.0 ML of Co. The Auger measurements were all made at 82 K. The 140, 150, and 160 K curves are all shifted upward in energy so that they can be viewed on the same plot.

peaks, but at higher temperatures the two peaks start to merge together and eventually become indistinguishable. These changes are likely to reflect the chemical shift of the valence band levels of the metals that would accompany the alloying process. These results indicate that the enlargement of the Co islands is the only rearrangement of Co adatoms that occurs when the annealing temperature is kept below 140 K and that intermixing between the Fe and Co atoms in the surface region begins at higher temperatures.

It would clearly be ideal to have a series of STM images taken at various temperatures between 110 K and room temperature. This would make it possible to follow the growth of the Co islands as the sample is annealed and, perhaps, allow us to directly connect a particular island size with the first magnetic transition. Upon taking such a series of STM images, we found a steady increase in the Co island size as the sample was annealed. Unfortunately, the long duration of this type of experiment rendered results that were quantitatively unreliable since residual gasses began to adsorb on the sample surface, decreasing the mobility of the Co adatoms.

Neither of the observed magnetic transitions is due to structural changes in the Fe films, or connected to contamination by the residual gasses in the vacuum system. It is well known that small changes in the dimensions of the unit cell of fcc Fe lead to drastic changes in the magnetic moment [1-2]. For this reason, the possibility of cobalt-induced structural changes can be ruled out due to the fact that no significant changes in the total moment of the system were observed as Co atoms were added to the bare films. Likewise, temperature-induced structural changes are highly improbable since the Fe films were deposited at 300 K. Ninety-minute exposures

(less than 0.6 Langmuir, where $1 \text{ L} = 10^{-6} \text{ Torr-sec}$) of the sample to the background gasses in the vacuum system were found to have barely noticeable effects on the net moment or magnetization direction of the films.

Based on our STM and AES studies, we propose that the initial perpendicular to in-plane SRT is due to a Co island growth effect. This is backed by our *ab-initio* studies that show that grouping the Co atoms together, as one does when annealing the sample above the temperature at which it was prepared, tends to increase the in-plane anisotropy. These calculations illustrate this tendency by considering the two distributions of 0.5 atomic layers of Co on an Fe film shown in Figs. 3.16(a) and 3.16(b). The first distribution models the situation in which the Co atoms group together as little as possible. In this case, the Co atoms are evenly spaced monomers that are arranged in a $c(2 \times 2)$ structure. In the second case, shown in 3.16(b), the Co atoms are grouped together as much as possible. Here, the Co islands are so large that it is possible to treat the anisotropy of the whole system as a combination of contributions from the bare area [simulated in calculations by the Fe/Cu(100) clean surface] and from the fully covered area [simulated by a monolayer of Co on Fe/Cu(100)].

The *ab-initio* calculations determine the electronic band structure and anisotropy energy using the all electron full potential linearized augmented plane wave (FLAPW) method [25] within the generalized gradient approximation (GGA) [26]. As the phrase *ab-initio* implies, the quantities yielded by these calculations are derived from first principles, or without empirical input or data-fitting parameters.

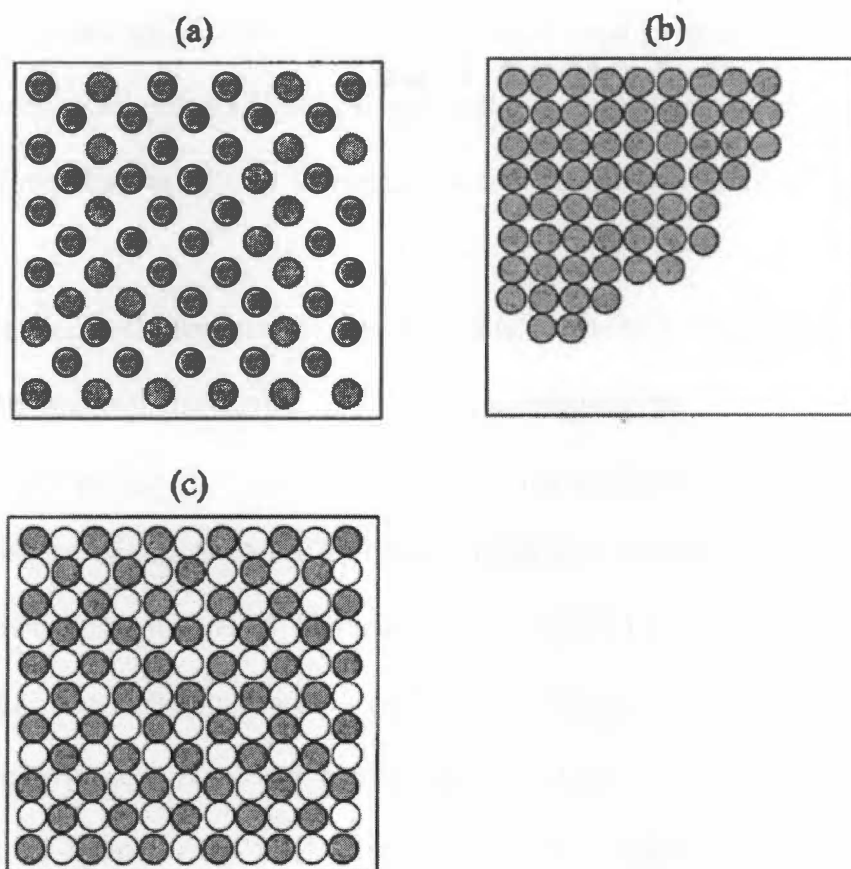


Figure 3.16: Limiting cases considered in ab-initio calculations of the magnetic behavior of Co-capped Fe/Cu(100). (a) The Co atoms are distributed evenly, in a $c(2 \times 2)$ structure. (b) The cobalt atoms are grouped together, forming a surface of bare Fe(100) and (1×1) Co regions. (c) An ordered $\text{Fe}_{0.5}\text{Co}_{0.5}$ alloy.

GGA is arguably the best approach within so-called density functional theory to calculate the ground state properties of atoms, molecules, and solids. In GGA, the energy due to non-Coulombic interactions between electrons (like exchange and correlation) is assumed to have a functional dependence on the charge and spin densities and their gradients. In other approaches, like the local spin-density approximation (LSD or LDA), the first derivatives of the charge and spin densities are not considered.

The results predict that in-plane anisotropy is energetically more favorable when the Co atoms are grouped together. The calculated magneto-crystalline anisotropy energies are $+0.78 \text{ erg/cm}^2$, -0.60 erg/cm^2 , and $+0.33 \text{ erg/cm}^2$ per atom for the Fe/Cu(100) surface when it is clean, capped by 1.0 Co-ML, and capped by 0.5 Co-ML arranged in a $c(2 \times 2)$ structure, respectively [27]. By our sign convention, a positive (negative) sign implies a tendency toward perpendicular (in-plane) magnetization. The 0.5 Co-ML covered system has a *less positive* magneto-crystalline anisotropy energy of $+0.09 \text{ erg/cm}^2$ when it is treated as a linear combination of large Co patches and bare Fe areas [28]. Clearly, the energies are very sensitive to the atomic arrangement. These results show that grouping the Co atoms together tends to make the contribution of the magneto-crystalline anisotropy less positive, or less able to overcome the in-plane shape anisotropy of the system.

The situation that we have observed experimentally is just an interpolation of the two endpoints considered in these calculations. While the samples considered in the calculations do not have the exact atomic arrangement of our experimental structures, the results obtained from them help us to understand the unexpected

tendency for grouping the Co atoms together to push the magnetization of the system toward the in-plane direction. At low temperatures, as shown in the STM image in Fig. 3.14(a), the Co atoms form small islands and are spread out more evenly than they are at higher temperatures. As the system is annealed, the Co atoms begin to cluster together and the sample ends up in a state that is relatively more like the configuration shown in 3.16(b), which has higher in-plane anisotropy.

The reverse SRT that occurs at higher temperatures is likely to result from alloying or intermixing the Fe and Co atoms at the surface. Our Auger studies indicate that the Fe and Co begin to alloy at these temperatures, and further *ab-initio* studies show that this intermixing these atoms at the interface tends to increase the perpendicular anisotropy of the system. For the extreme configuration of an ordered FeCo alloy, as shown in Fig. 3.16(c), the calculated magneto-crystalline anisotropy is $+1.29 \text{ erg/cm}^2$, indicating a strong tendency toward perpendicular anisotropy.

We have observed an unusual progression of SRTs in the cobalt capped Fe/Cu(100) ultrathin film system that results from the rearrangement of the cobalt atoms as the system is annealed. The details of the reconfiguration of the Co atoms have been observed experimentally and *ab-initio* calculations have qualitatively explained the effects of the new configurations of the Co atoms on the magnetic properties of the system.

3.2 Wire Arrays: The effect of alloying on magnetic ordering

In this section, we investigate arrays of parallel $\text{Fe}_{1-x}\text{Co}_x$ alloy nanowires that have been prepared along the atomic step edges of a miscut W(110) surface. Their magnetic properties have been studied with the surface magneto-optical Kerr effect (SMOKE) as a function of the relative concentration of the two materials. At low (< 35%) cobalt concentrations, the wire arrays exhibit a ferromagnetic easy axis along the substrate $[1\ -1\ 0]$ direction, which is in the surface plane, but perpendicular to the wires. Unlike the bulk alloy, this system shows a decrease in its Curie temperature as cobalt is added to pure Fe. The Curie temperature drops sharply near $x = 0.35$, indicating that cobalt frustrates magnetic ordering in the system.

3.2.1 Introduction

A major goal in recent years has been to make magnetic and electronic devices that function on the nanometer scale. In the past two decades, important advances have been made through the study of two-dimensional films, including the discovery of the giant magneto-resistance effect that has already been applied in devices like spin-valve read sensors for disc drives and in spin-tunneling devices for non-volatile random access memory. As efforts to reduce device size scales have continued, it has become increasingly attractive to investigate quasi one-dimensional magnetic nanowires that are as small as one to several tens of atoms in diameter.

The nearly perfect step flow growth exhibited by iron on the W(110) surface has led to significant progress in the study of magnetic nanowires. Parallel arrays of one- and two-monolayer high ribbons of Fe, which are larger than the magnetic domain size along only one direction, can be formed at elevated temperatures on the W(110) surface if it is purposely miscut. This has made it possible to investigate the dependence of the coupling between quasi one-dimensional wires on their width and separation [29-30]. In addition, the magnetic domain structure of the nanowires has been imaged with impressive, sub-nanometer resolution with spin-polarized scanning tunneling spectroscopy [31-32]. An example of this work can be found in Fig. 1.9 in Chapter One.

While most of the ongoing work on magnetic nanowires has focused on single element materials [29-35], it is potentially useful to explore the tunability of these nanostructures by studying bi-metallic alloy materials. In this article, we report on the magnetic behavior of parallel arrays of $\text{Fe}_{1-x}\text{Co}_x$ alloy nanowires that are prepared via the step-flow mechanism on a vicinal W(110) substrate. The properties of the bulk alloy have been well studied [3]. Its phase diagram is shown in Fig. 3.17. At cobalt concentrations below ~25%, the Curie temperature is reached below the α -phase to γ -phase structural transition temperature and increases about 7 °C per percent of added cobalt. At Co concentrations between 25% and 73%, the structural transition to the non-magnetic γ -phase occurs while the α -phase is still ferromagnetic, leading to a so-called "virtual Curie temperature" for the α -phase that exceeds the structural transition temperature. Mean-field calculations have predicted a large

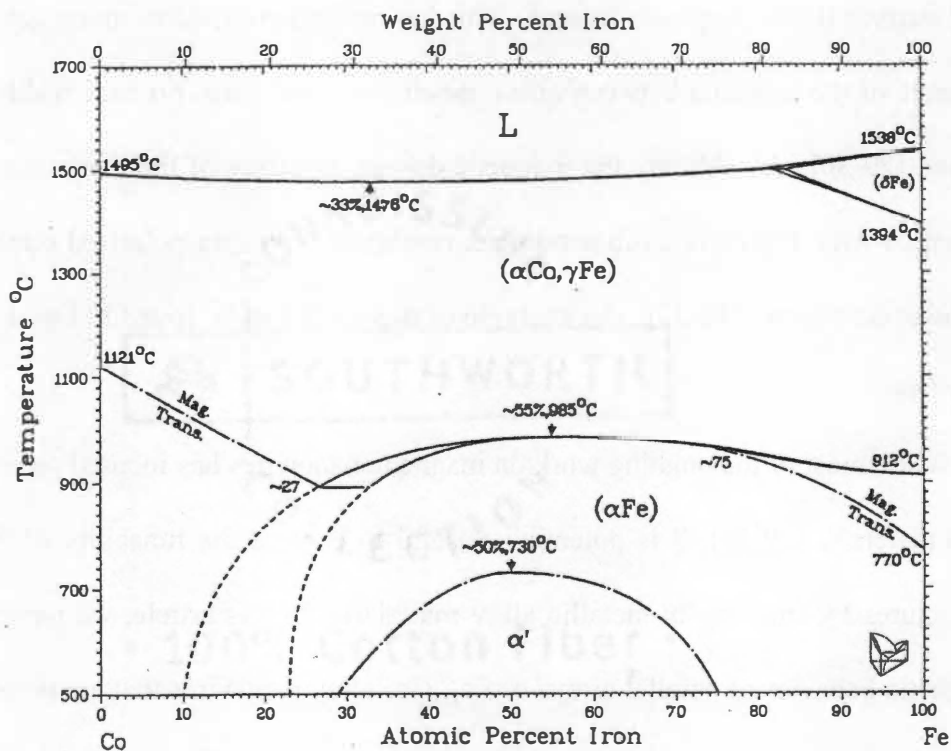


Figure 3.17: Phase diagram for bulk FeCo alloys [from ref. 3]. The right side of this phase diagram shows that as Co is added to pure Fe in the bulk alloy, the Curie temperature (denoted by "Mag. Trans.") increases. This is opposite to the behavior that is observed in FeCo alloy nanowires on W(110). We note here that the right axis of the plot shows that the γ -Fe phase only exists above the Curie temperature of pure Fe, as we discussed in our treatment of fcc Fe films on Cu(100) at the beginning of this chapter.

maximum in the virtual Curie temperature for equiatomic FeCo [36]. Our measurements show a drastically different phase diagram for this alloy when it is grown as atomic nanowires on W(110). Initially, the Curie temperature falls approximately one degree per 1% of added cobalt. It decreases more dramatically as the Co concentration is increased beyond 35% and it is likely that the equiatomic alloy is non-magnetic.

3.2.2 *Synthesis and magnetic properties of FeCo alloy nanowires on W(110)*

Experiments were performed in an ultrahigh-vacuum system with a base pressure of 8.0×10^{-11} Torr. The tungsten substrate was subjected to cycles of heating to 1200°C in a 1.0×10^{-7} Torr oxygen atmosphere in order to drive carbon contamination out of the surface region followed by flashing to 2400°C to sublimate surface oxide layers and other contaminants. This process was repeated until carbon superstructure spots vanished from the LEED pattern and clean Auger spectra were observed. Once the surface was cleaned in this way, flashing the sample to 2400°C was sufficient to prepare a clean template at the beginning of each experiment. The width of the parallel W(110) terraces was determined by spot profile analysis of the electron diffraction pattern (SPA-LEED). The LEED pattern and splitting of the (0,0) diffraction spot due to the presence of the parallel terraces is given in Fig. 3.18(a). As described in [37-38], the terrace width (d), the lattice constant ($a = 0.3158$ nm), and the corresponding distances in the LEED pattern (ΔK and K , respectively) are simply related in this way:

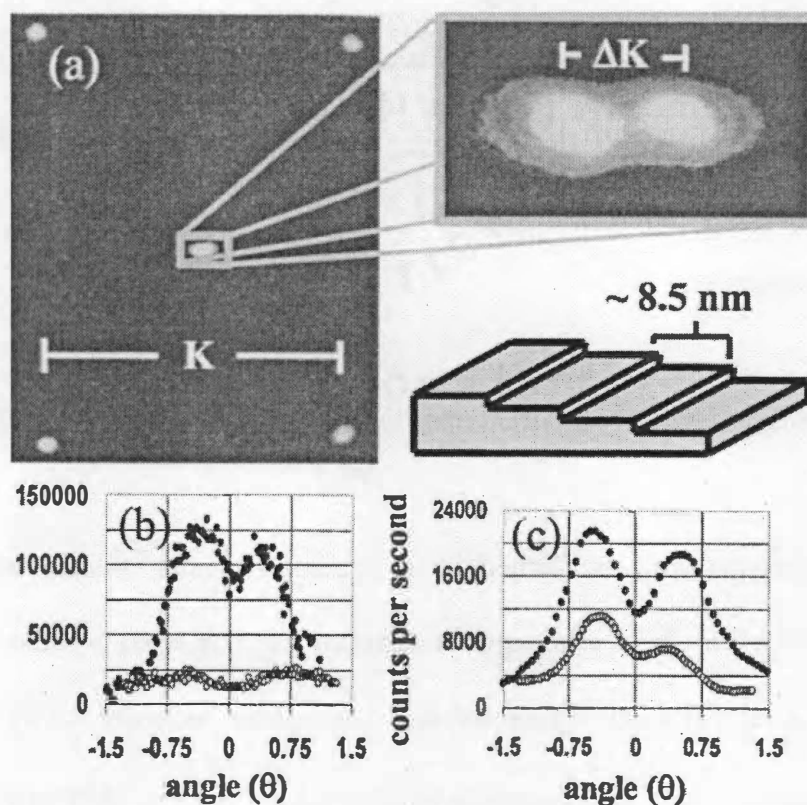


Figure 3.18: SPA-LEED measurements of a stepped W(110) surface. (a) Low energy electron diffraction (LEED) pattern of a freshly prepared vicinal W(110) substrate. This pattern was captured at 321 eV. The spot splitting (ΔK) shows that the surface is made up of parallel atomic steps with edges along the $[0\ 0\ 1]$ direction. The ratio of relevant distances in the LEED pattern allows us to calculate the average terrace width, as described in the text. Intensity profiles of the (0,0) diffraction spot for a 0.7 ML Fe overlayer and a 0.51 ML Co overlayer are presented in (b) and (c), respectively. The open circles represent data taken at 298 K, immediately after deposition. The filled circles are data recorded after annealing to 750 K for 5 minutes. The difference in the noise level in the two plots arises from taking the data from a pixelated 2-D profile of the spot (b) and running our acquisition system in a 1-D line scan mode (c). The heights and widths of the peaks are not significantly affected.

$$\frac{d}{a} = \frac{\sqrt{2}}{2} \frac{K}{\Delta K}$$

This equation is simply illustrating the reciprocal relationship between distances in real space, and distances observed in diffraction patterns. The splitting ΔK is inversely proportional to the wire spacing (d) that caused it. The same relationship holds for the distance between adjacent atoms ($2a/\sqrt{2}$) along the $[1 -1 0]$ direction and the distance K in the diffraction pattern. This analysis revealed that the average step height was ≈ 8.5 nm and that the step edges were indeed parallel to the $[001]$ direction.

Iron was deposited by e -beam evaporation of a 99.995% pure Fe wire and the cobalt was dosed by heating a molybdenum crucible filled with pieces of a 99.9975% pure Co wire in the same way. The rate of deposition was controlled in each case by flux monitors that were mounted on each source. As was the case in our studies of Fe films on Cu(100), the deposition rate for a given flux monitor reading was, in turn, calibrated by using the adsorbate to substrate Auger intensity ratios. The trick was to determine the correspondence between Auger intensities (Fig. 3.19) and absolute coverage. In the case of iron on W(110), a magnetic behavior that occurs in a narrow thickness window around 1.48 atomic layers was used to establish the doser rate. Figure 3.20, obtained from reference [39], shows that at 0.58 ML, Fe films on W(110) become ferromagnetic. Between 1.20 ML and 1.48 ML, no magnetic signal is observed. (This absence of magnetic signal was later found to be due to the fact that Fe/W(110) films develop an extremely high coercivity in this thickness regime

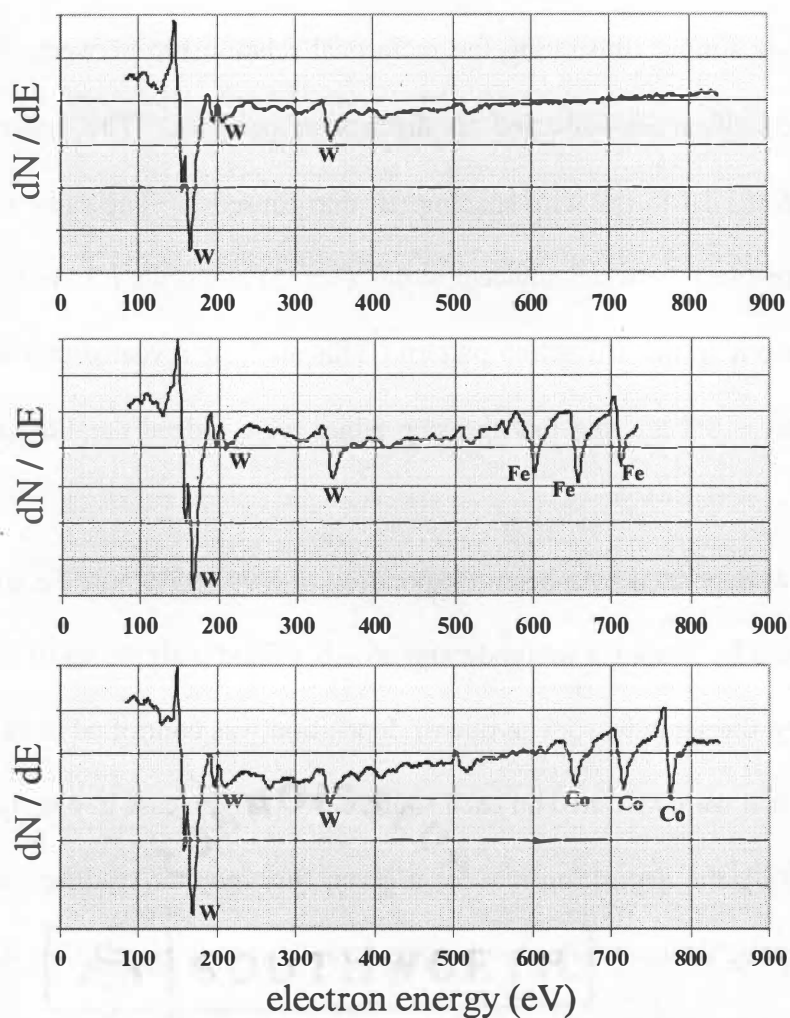


Figure 3.19: Auger electron spectra for clean, Fe-capped, and Co-capped W(110). The spectra correspond to the W(110) substrate (a) after flashing it to 2400 °C, (b) after depositing 0.7 ML Fe, and (c) after depositing 1.0 ML Co.

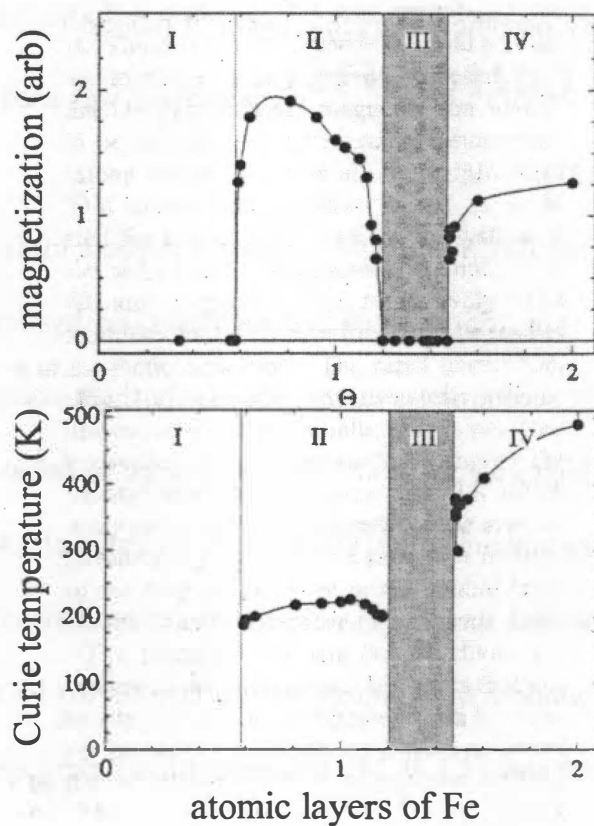


Figure 3.20: Magnetic signature from Fe/W(110) that was used to calibrate absolute Fe coverage [from ref. 39]. These plots show the coverage dependence of (a) the polarization asymmetry of scattered electrons (an effect known to be roughly proportional to magnetization [40]) and (b) the Curie temperature of the Fe/W(110) system. The coverage scale in this plot was established with scanning tunneling microscopy, which is the best method for determining absolute coverage of atomic layer films. Observing the sudden reappearance of magnetic signal that occurs at 1.48 ML allowed us to establish an absolute value for the Fe coverage in our studies of this system.

[41]. The authors in [39] couldn't observe magnetic response here because their field wasn't high enough to drive the moments to a particular direction.) At 1.48 ML, hysteresis loops suddenly become observable again at modest (< 2000 Oe) applied fields. It is the observation of this magnetic signature that was used to calibrate the Fe doser rate (see Fig. 3.21).

With a fixed Fe ion flux, I was able to observe in-plane hysteresis loops after an Fe dose of 85 sec. For 155 and 165 second doses, no hysteresis loops were observable. After a 170 second dose, easily observable, high-coercivity hysteresis loop reappeared. The high coercivity and sudden change in behavior is precisely what was described by the authors in [39] and [41]. If the value of 1.48 ML quoted in [39] was exact, then the fact that I was able to locate the magnetic phenomenon within a 5 second time window would mean that the error in the Fe thickness would be $\sim 3\%$. Given that the value of 1.48 ML was determined more realistic figure for the error in the absolute Fe thickness is $\sim 10\%$. The error in *relative* thickness is much lower, as it is determined by the dose time, which could be controlled to within 0.1-0.2 seconds with a stopwatch and the manually controlled shutter.

The cobalt (775 eV) to tungsten (169 eV) Auger ratio was assigned to an absolute coverage by tedious (twice as many data points) reproductions of the Auger uptake curves recorded in [42]. Johnson *et al.* established that the first elbow, or slope break, in the Auger buildup curve shown in Fig. 3.22 corresponds to completion of the growth of the first atomic layer of a Co/W(110) film. Two reproductions (Fig. 3.23) of this curve revealed slope changes at the same Co/W Auger peak ratio of 0.5. The break point can only be determined within ± 30 seconds, resulting in an error in

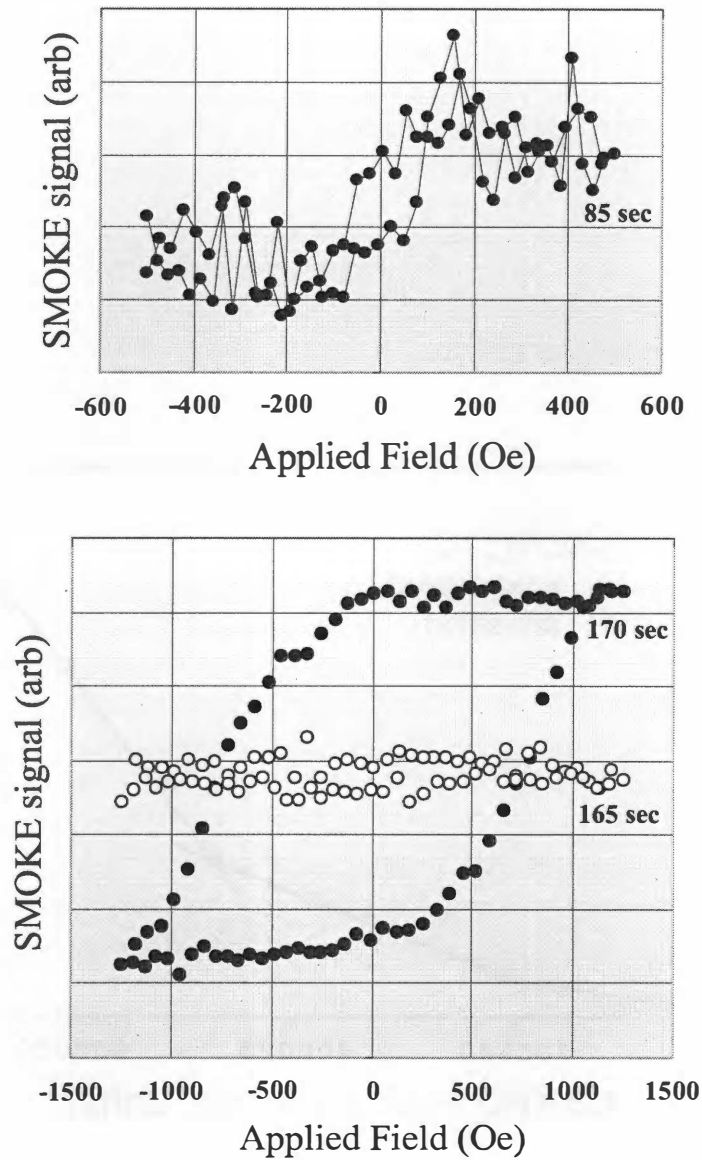


Figure 3.21: SMOKE magnetization curves for room-temperature-grown Fe/W(110). Each of the three curves were recorded at 90 K. Only the duration of the Fe dose was changed in each case. The sharp change in the magnetic behavior of the film that occurs between the 165 second and 170 second Fe doses indicates that a dose time between 165 and 170 seconds corresponds to a film thickness of 1.48 atomic layers.

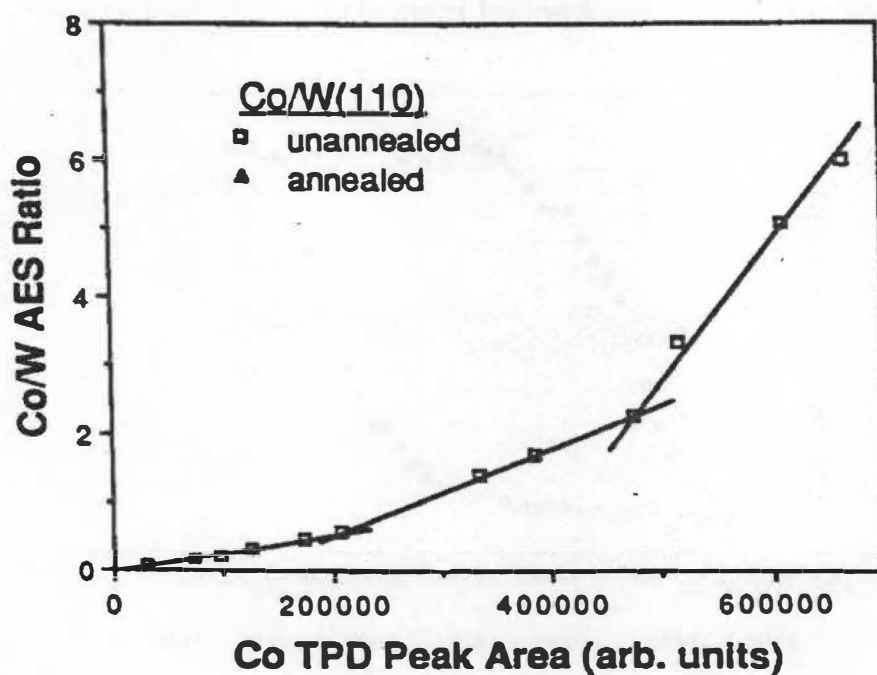


Figure 3.22: The dependence of the Co(775)/W(169) Auger peak ratio on coverage [from ref. 42]. Thermal programmed desorption (TPD) is a technique in which a substrate is heated to a temperature that is high enough to result in desorption of overlayer atoms. A fixed fraction of the desorbed atoms are detected with a pressure gauge or mass spectrometer. The area under a TPD spectrum, or "TPD peak" is known to be directly proportional to overlayer coverage. The first break in the slope of this plot is found to correspond to the presence of 1 ML Co in [42].

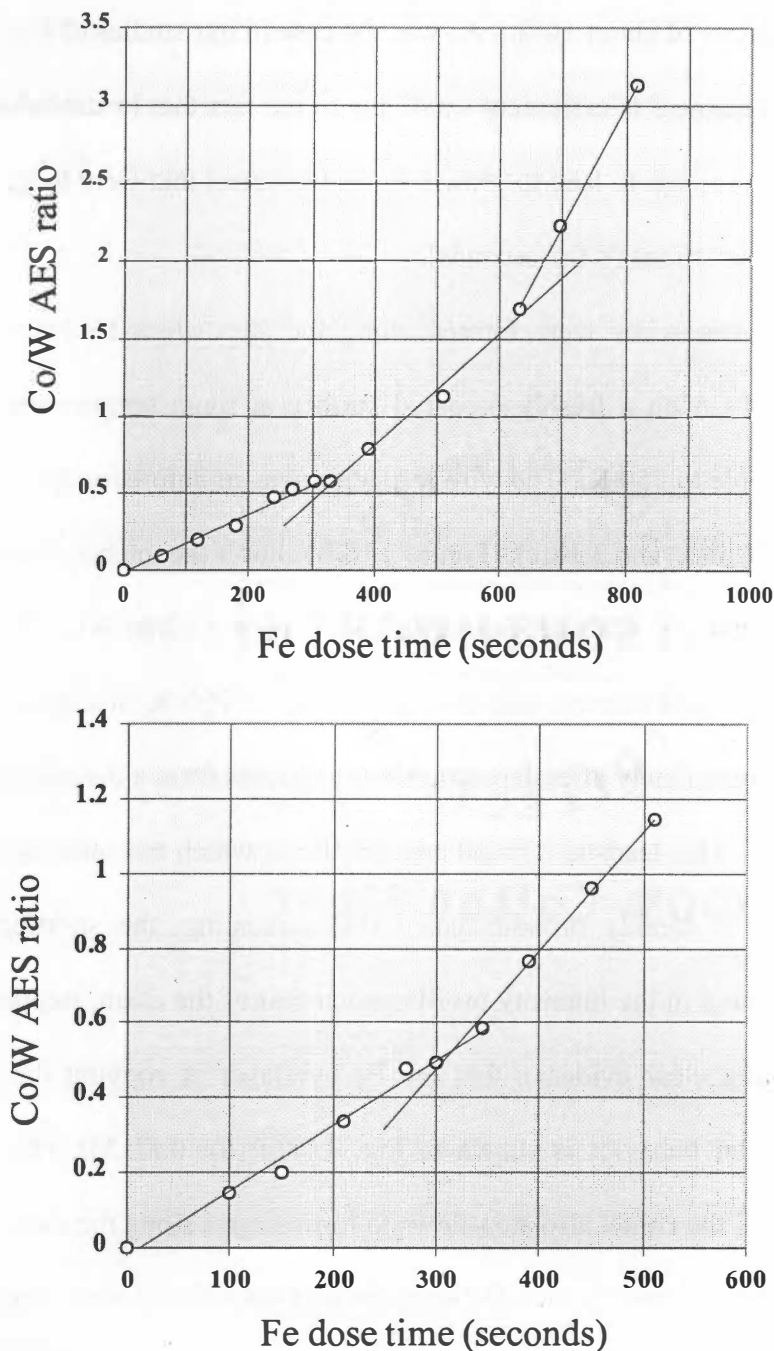


Figure 3.23: Auger uptake curves for Co/W(110). The plots show the results of two experiments in which the discontinuity in the slope of the dependence of the Co(775)/W(169) Auger peak ratio on coverage was reproduced. As in the experiment shown in the previous figure, the first break in the slope occurred when the ratio was approximately 0.5. These curves allowed us to determine the rate of our Co doser to be approximately 1 ML per 300 sec. Rescaling the horizontal axis of this plot to units of monolayers gave us the relationship between the Co/W AES ratio and Co coverage, which was used daily to confirm that the doser rate remained constant.

absolute Co thickness of about 10%. As was the case in our studies of Fe on Cu, the error in *relative* thickness is extremely small due to the fact that I established a doser rate that was slow enough to lead to growth times (minutes) that were long compared to the error in growth times (< 0.2 seconds).

The alloy nanowires were formed along the step edges by simultaneously depositing Fe and Co on a freshly prepared surface at room temperature and then annealing the sample to 750 K. The wire formation was monitored with SPA-LEED, as shown in Fig. 3.18(b) and 3.18(c). Figure 3.18(b) shows the intensity profile of the (0,0) diffraction spot just after depositing 0.7 ML Fe on a clean W(110) surface at room temperature (open circles) and after annealing to 750 K to create nanowires (filled circles). Immediately after deposition, the Fe atoms form a disordered network of islands [29,43]. This leads to a broad spot profile in which the splitting due to the stepped substrate is weakly pronounced. After annealing, the splitting and the absolute values found in the intensity profile match that of the clean, stepped W(110) substrate, providing clear evidence that the Fe overlayer is copying the substrate. Qualitatively similar behavior is shown in Fig. 3.18(c) for 0.51 ML of Co on this surface. Evidently, the cobalt also step-flows to form stripes along the step edges.

After the wires were formed, the samples were cooled and placed into position for surface magneto-optical Kerr effect (SMOKE) measurements. In the experiments that will be discussed here, the total overlayer coverage was fixed at 0.7 atomic layers. Only the relative concentrations of Fe and Co were varied. In each case, the easy magnetization axis was found to lie along the $[1 \ -1 \ 0]$ direction, which is in the plane of the wires, but perpendicular to them. The fact that this is also the easy

magnetization direction for pure Fe and Co ultrathin films [43-45] supports the speculation that surface induced anisotropy is more important than shape (dipolar) anisotropy in these structures. Representative magnetization curves that were recorded with the applied field along the easy axis are displayed in Fig. 3.24. In this geometry, the magnetization curves that we observed were nearly always square hysteresis loops, such that the remnant and saturation Kerr intensities were equal until the system was heated to about 15 degrees below its Curie temperature.

In Fig. 3.25, the temperature dependence of the remanent Kerr signal is given for samples of various relative concentrations. By finding the temperatures at which the remanent signal vanished, we were able to determine the ordering temperatures given in Fig. 3.26. The ordering temperature for the pure Fe wires is in reasonable agreement with that found for the same coverage in [30]. In stark contrast to the bulk phase diagram for the FeCo alloy, the Curie temperature decreases as the Co concentration is increased, and falls rapidly after the concentration reaches 30%.

It is evident that the addition of cobalt inhibits the magnetic order in the system. In fact, given the relationship between the Curie temperature and the Co concentration shown in Fig. 3.26, it is questionable whether or not this system is ferromagnetic at all for Co concentrations greater than 50%. No evidence of ferromagnetism was found in the system above 67 K (our lowest cooling temperature) for cobalt concentrations above those shown in the figure.

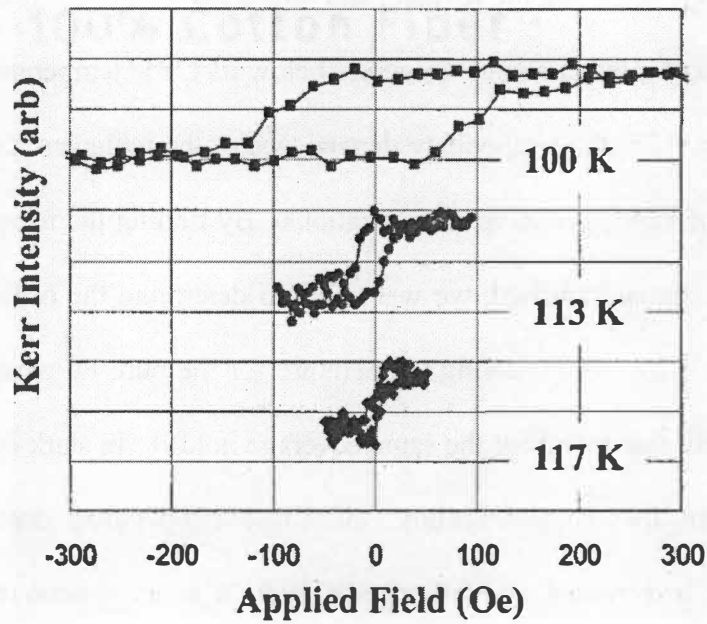


Figure 3.24: Typical temperature dependent behavior for surface magneto-optical Kerr effect hysteresis loops for the nanowire arrays. In this case, the wires were made from 0.7 atomic layers of an $\text{Fe}_{0.79}\text{Co}_{0.21}$ alloy. The loops were recorded with the applied field along the $[1\ -1\ 0]$ direction.

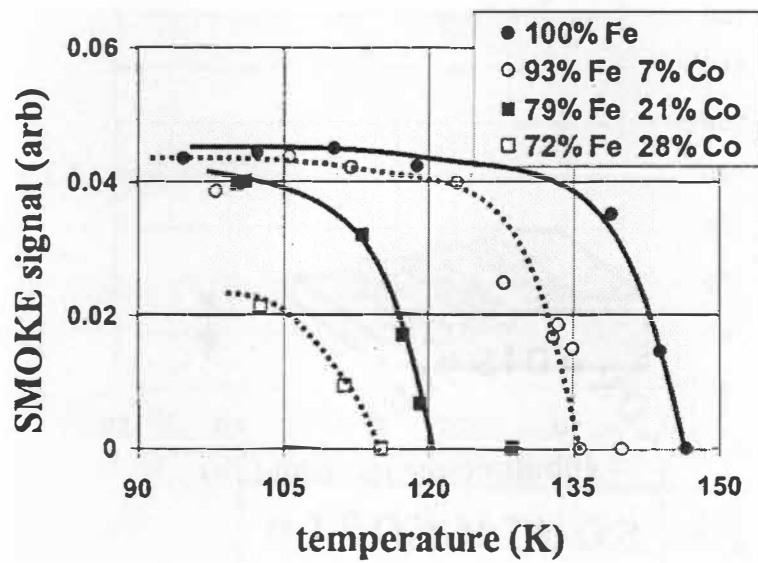


Figure 3.25: Temperature dependence of the remanent magnetization observed in longitudinal Kerr hysteresis loops for 0.7 ML FeCo alloy nanowires.

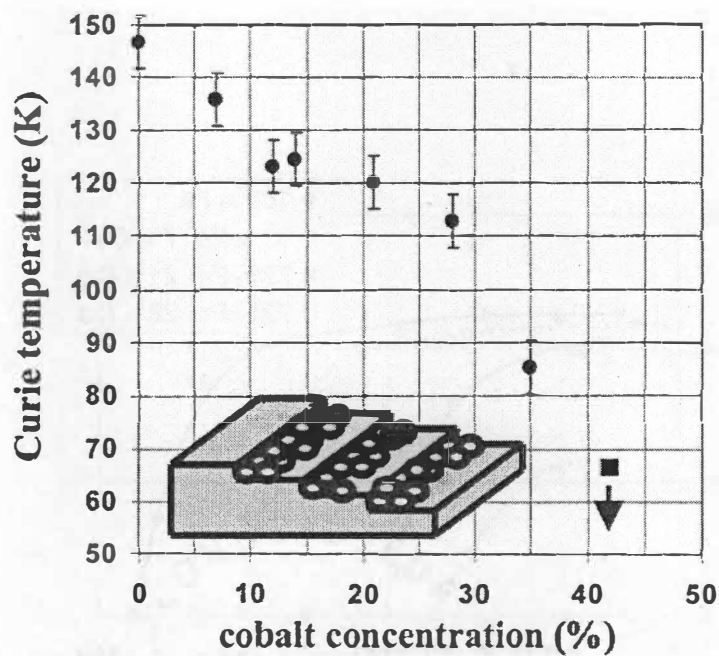


Figure 3.26: Dependence of the Curie temperature of the alloy nanowire system on the Co concentration. The Curie temperature that corresponds to the last (square) data point must lie below the temperature shown. No hysteresis was observed at or above 67 K, which was our lowest achievable temperature.

3.2.3 Discussion

It is striking that cobalt, as a ferromagnetic element, suppresses ferromagnetic order in this system, particularly in light of the fact that such behavior has never been observed in the bulk FeCo alloy. Originally, it was thought to be possible that, in the nanowire configuration on W(110), there is phase separation of the elements that make up the FeCo alloy. Because we did not perform STM studies of the nanowires, we could not rule out this effect. Although Fe and Co are completely miscible in bulk, phase separation has been observed at the surface of an ordered B2 FeCo alloy [46].

In the case of extreme phase separation, the Fe and Co would contribute separately to the overall magnetic behavior of the system. Since Curie temperature vs. thickness plots, as in Fig. 3.27, suggest that pure cobalt is magnetically "dead" in the sub-monolayer regime on W(110) [45], phase separation may explain why the behavior and Curie temperatures of these alloy nanowires are so similar to the *pure Fe* wires studied in ref. [31], in which T_c decreased as the Fe dosage was decreased. This similarity between the Fe dose dependence of the ordering temperature of *pure Fe* wires and $\text{Fe}_{1-x}\text{Co}_x$ alloy wires is evident in Fig. 3.28. The $\text{Fe}_{1-x}\text{Co}_x$ nanowire system behaves as if the Co is contributing very little to the ferromagnetic ordering in the system.

Very recently, a German group [47] repeated our magnetic measurements [48] and performed additional STM studies of this alloy nanowire system. Their magnetic measurements reproduced our findings and their STM images revealed that it is most

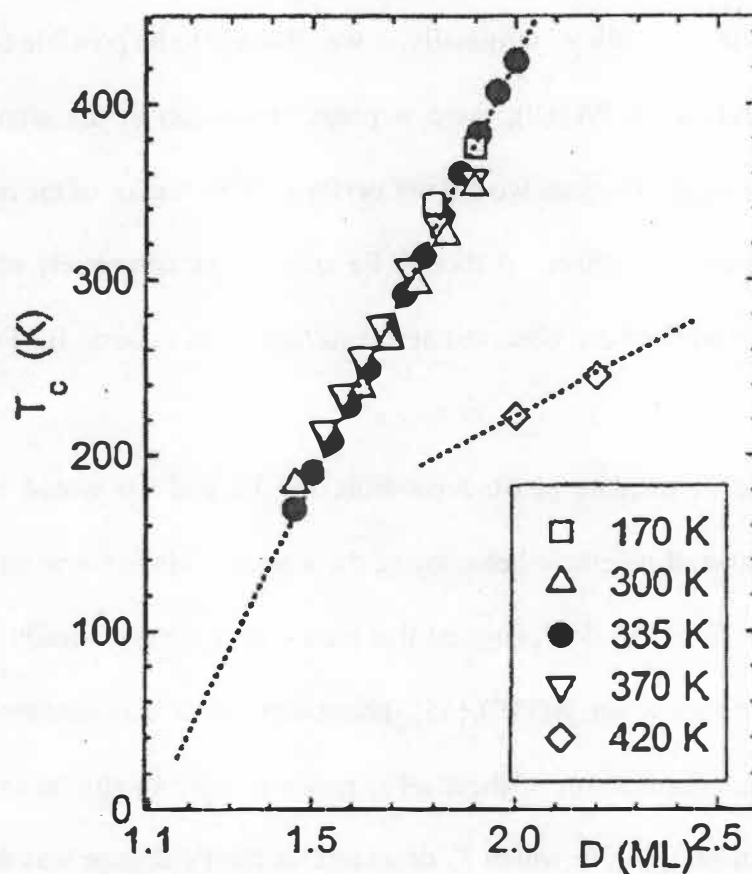


Figure 3.27: Dependence of the Curie temperature of a Co/W(110) film on film thickness [from ref. 45]. At least two groups have speculated that the first atomic layer of Co may be magnetically "dead" on this substrate [44-45]. The extrapolation in this plot from ref. [45] implies that films grown at temperatures below 420 K will be magnetically "dead" (i.e. have a Curie temperature of 0) when they are thinner than 1.1 atomic layers. The fact that I find no magnetic signal for 0.7 atomic layers of pure Co on W(110) at 67 K supports this speculation.

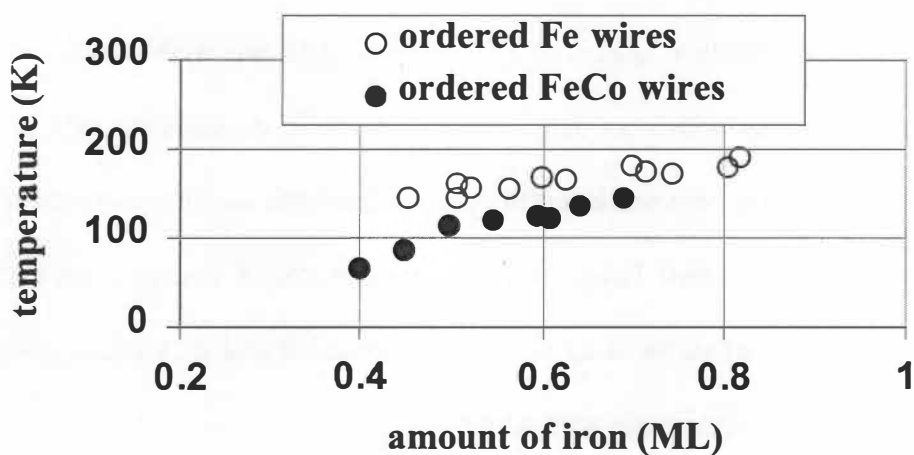


Figure 3.28: Comparison of the Curie temperatures of pure Fe and alloyed FeCo nanowires. I have included my data in this plot by considering only the iron present in the alloy nanowires, which, again, always consisted of 0.7 ML of $\text{Fe}_{1-x}\text{Co}_x$. The data for the pure Fe wires is taken directly from ref. [29]. The similarity between the magnetic behaviors of the two systems is surprising. The alloyed system behaves as if the cobalt is either hindering or not taking part in the magnetic ordering. If the latter is true, the small offset between my data and that taken by Elmers *et al.* can be explained by a small difference in our thickness calibrations and/or measured temperatures.

likely that the Fe and Co do *not* segregate when grown as nanostripes. Their results indicate that the reduction of the Curie temperature that occurs as Co is added to the system is an intrinsic property of the nanostructured alloy on W(110). Based on previously calculated electronic energy band structures for bulk Fe and Fe films on W(110), the authors in ref. [47] posed a reasonable argument for the difference in the behavior of the bulk and nanowire manifestations of the alloy. They pointed out that while adding Co to bulk Fe would *increase* the density of states of the system at the Fermi level (E_f), adding Co to monolayer-thick Fe structures on W(110) would actually *reduce* the density of states at E_f . According to the well-known "Stoner criterion," the extent to which an object is ferromagnetic depends directly on the strength of the coupling between electron spins (J) and the density of states at E_f . Unlike what is seen in the bulk FeCo alloys, the nanostructured system experiences a decrease in its density of states at E_f as more Co is added and its tendency toward magnetic order therefore *decreases* with added Co.

In summary, we have explored the dependence of the magnetic ordering temperature of $\text{Fe}_{1-x}\text{Co}_x$ alloy nanowire arrays on the relative concentrations of the two constituents. Unlike the bulk alloy, the addition of cobalt inhibits magnetic ordering in the nanostructured alloy system. The unusual new behavior provides a clear example of how the magnetic properties of a material can be tuned by nanostructuring it and altering the distribution of its electronic states.

Chapter 4

The Effects of Spatial Confinement on Magnetism

4.1 Introduction

One of the major challenges in developing an understanding of magnetic nanostructures that we discussed in Section 1.3 was coping with the fact that it is often the case that only one growth mode is thermodynamically favored for a particular material on a particular substrate. This has meant that in order to synthesize different types of nanostructures out of a single material, people have had to reach for different templates in each case. This has severely stunted the growth of our intuition about how nanostructuring affects the properties of materials. Changes in properties that are due to the differing templates have masked the intrinsic changes that are caused by nanostructuring. One consequence of this is that it has been impossible to systematically observe how forcing a material to form flat films, nanowires, and isolated dots affects its magnetic behavior.

In fact, forming magnetic nanostructures of *any* kind from iron on the Cu(111) surface is a particularly daunting task. Conventional growth techniques, like sputtering or thermal evaporation in ultra-high vacuum, can't produce ultrathin films, nanowires, or isolated dots from iron on this surface. This is because Fe has a strong tendency to form jagged, discontinuous, multi-layered islands on Cu(111) due, in part, to an effect called twinning. Twin structures are common features of epitaxial

growth on fcc(111) surfaces [1]. As shown in Fig. 4.1, the rhombic surface unit cell of the fcc(111) surface provides two possible sites, which we will call “A” and “B”, for adatom nucleation. Since the difference between the nucleation energies of the two sites is zero, an atom has no preference for one site over the other. Those that nucleate at A sites seed the growth of A-type islands, and those that nucleate at B sites lead to B-type islands. These two islands cannot merge to form a smooth film because a fault line, as shown in Fig. 4.1, always exists at the boundary between them.

A second feature that leads to roughness is low interlayer mass transport [2]. Because there is a high energy barrier for Fe atoms to overcome when moving from one atomic step to the next, the thermal motion of the atoms is unable to “heal” pits and peaks in the morphology. The combined consequences of fcc twinning and low interlayer mass transport can be seen in the STM image of an Fe/Cu(111) film shown in Fig. 4.2. The film was prepared by MBE at a substrate temperature of 220 K, with a nominal Fe dosage of 2 atomic layers. The marked line profile shows that the typical island height is about 5 ML, and that a considerable fraction of the copper surface (darkest contrast) remains uncovered after two atomic layers of Fe are deposited.

In the following sections, we will show the impact that our success in using a novel growth technique to produce iron quantum dots on Cu(111) has had in addressing this challenge of systematically observing the effects of nanostructuring. In this chapter, we’ll compare our results for the magnetic behavior of Fe quantum dots on Cu(111) with those for atomically smooth Fe films and nanowires made on

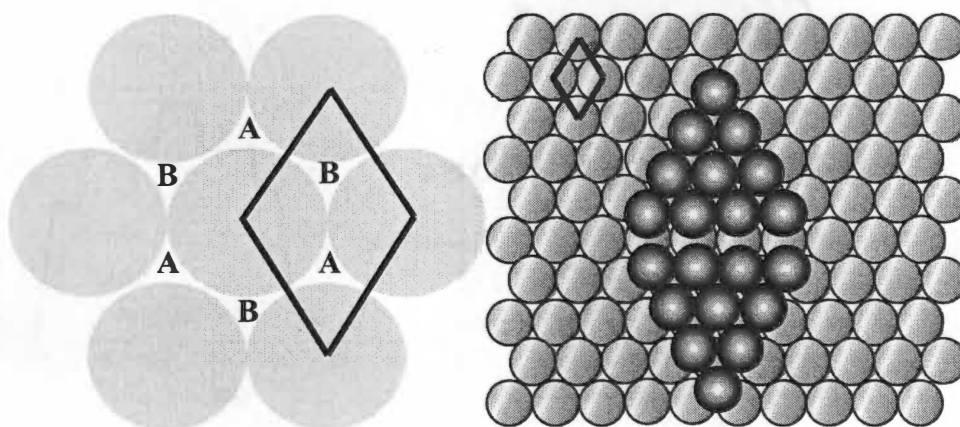


Figure 4.1: Schematics showing the phenomenon of twinning. The spacing between iron atoms on the Cu(111) surface is such that iron atoms in a particular island will either occupy "A" sites only or "B" sites only, depending on which of these two sites was settled upon by the atom that seeded the island. The image shows the fault line that forms when an A-type island tries to merge with a B-type island.

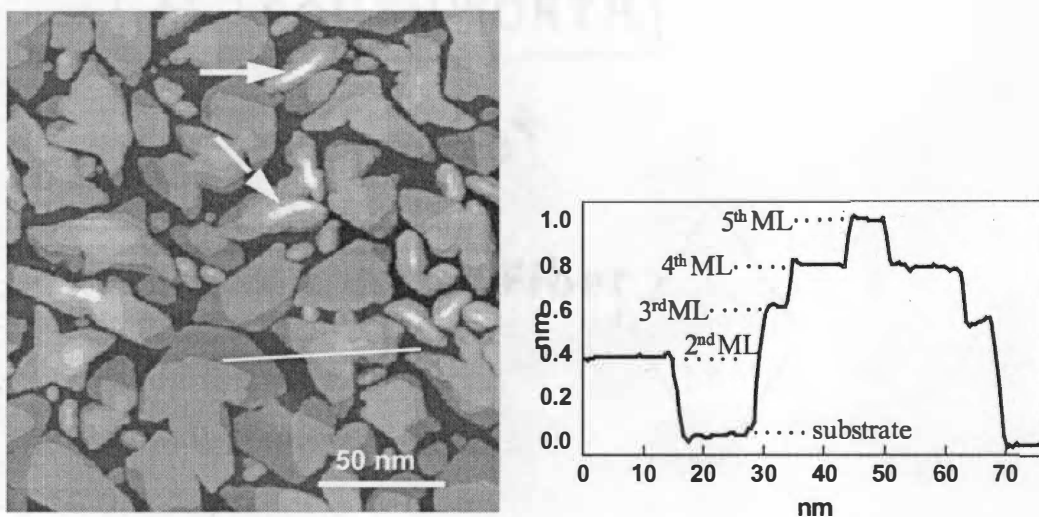


Figure 4.2: Conventional MBE growth of Fe on Cu(111) [from refs. 3 and 19]. The STM image (left) and line scan (right) show the morphology that results when 3.0 atomic layers of Fe are deposited on Cu(111) at room temperature. The morphology consists of isolated, multi-layered islands. The atomic structure of the film is fcc, but the arrows indicate locations where the film thickness has reached 6 ML and bcc ridge-like structures have formed. This effect also contributes to the rough morphology of thermal MBE-grown Fe films on this surface.

the same substrate from the same amount of material (0.8 atomic layers) [3]. STM images of the three manifestations of Fe are shown in Fig. 4.3. The magnetic measurements that we will present are the first direct observations of the effects of spatial confinement in one, two, and three directions for a sample in which the sample material, amount of sample material, and substrate were unchanged.

4.2 Dots: the effects of interparticle interactions on ordering temperature and magnetic stability

In the preceding chapter, we discussed ways in which we can control the magnetic behavior of two-dimensional films and one-dimensional nanowires. In the following, we continue this trend and focus on a magnetic system built of structures that are even further confined. Here, we will show how the magnetic behavior of a quasi “zero” dimensional magnetic system can be tailored.

We will begin by showing how a novel method can be used to produce assemblies of isolated Fe quantum dots on a Cu(111) surface. This growth mode has not been observed before for iron on copper. We find that the size and spacing of the quantum dots can be varied in a controlled manner by changing the growth parameters. This system is ideal for theoretical modeling in that the size, positions, and composition of the dots are precisely known. Through measuring the magnetic properties of the dot assemblies with SMOKE and Monte Carlo simulation of the magnetic behavior, we have found a way to determine the relative roles that dot-dot

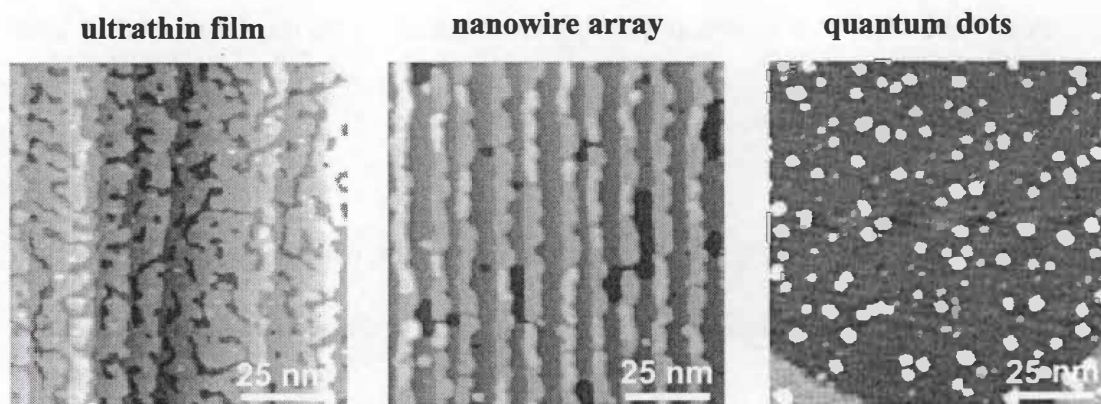


Figure 4.3: Three forms of iron nanostructures formed on the Cu(111) surface. The film, wire array, and dot assembly each consist of the same amount of material -- 0.8 atomic layers of iron atoms. The ultrathin film was prepared with pulsed-laser deposition. The material in the nanowire array was dosed via conventional molecular beam epitaxy and self-assembled through step-edge decoration. The quantum dot assembly was formed using a buffer-layer-assisted growth technique.

interactions and the magnetic anisotropy of the dots play in the magnetic stability of the system.

4.2.1 Synthesis of Fe quantum dots on Cu(111)

The formation of quantum dots of Ag on a silicon surface with a buffer layer assisted growth (BLAG) process has recently been demonstrated [4]. Two crucial steps are involved in the BLAG process: (1) Quantum dots are formed on top of an inert gas buffer layer that has been frozen onto a substrate. (2) The buffer layer is evaporated away, allowing the formed quantum dots to land on the substrate. A cartoon depicting this process is shown in Fig. 4.4. The first step of the process is rather straightforward since, due to the low surface free energy of the inert gas layer, the deposited material tends to form clusters, rather than wet the surface. The second step is rather brutal and can drastically affect the spatial and size distributions of the original assembly of nanoparticles. Moreover, depending on the strength of the interaction between the quantum dots and the substrate, the assembly may not be stable after landing on the surface and could subsequently decay into multilayer islands or even two-dimensional films.

Whether or not the BLAG method can be used as a general method for forming magnetic quantum dot arrays is of great interest. In several systems (Fe/W(110) [5] and Fe/Cu(111) [6] are two examples), the magnetic properties of two-dimensional films and one-dimensional nanowires have been measured. While, depending on the substrate miscut and deposition rate, it is possible to form two-

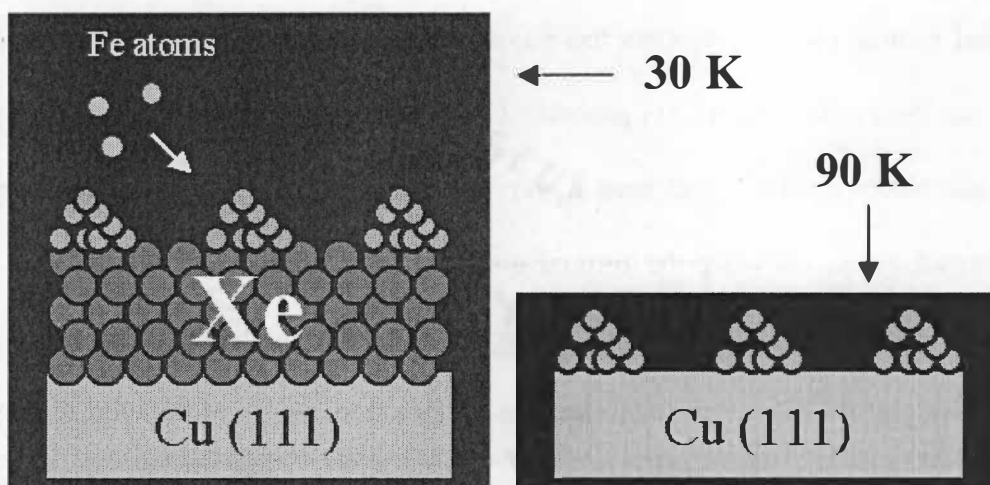


Figure 4.4: Buffer-layer-assisted growth. First, a substrate is prepared in ultrahigh vacuum and cooled below 30 K. Xenon gas is then leaked into the chamber. When it comes into contact with the cold substrate (Cu(111) in this case), it condenses on the surface. Since Xe is such an inert substance, atoms of other materials that are subsequently deposited tend to stick to each other and form clusters instead of spreading out over the surface of the xenon. As shown in the picture on the right, raising the temperature of the system to 90 K causes the Xe to sublime, leaving isolated clusters on the substrate.

dimensional films or 1-D nanowire arrays on these surfaces, conventional deposition techniques do not yield quantum dots. With the ability to grow “zero-dimensional” Fe quantum dots on these surfaces would come the opportunity to conduct systematic studies of the effects of reduced dimensionality on the magnetic properties of these systems.

To understand and predict the magnetic behavior of an assembly of zero-dimensional nanoparticles, it is imperative to have accurate knowledge of their chemical makeup, size distribution, and spatial arrangement. It is well known that small variations in the radii of the nanoparticles cause large changes in the time dependent magnetization and blocking temperature of these systems [7-9]. Clearly, the relative positions of the particles determine to what extent particle-particle interactions drive the magnetic behavior of the assembly. With this in mind, quantum dot assemblies prepared under ultra-high vacuum (UHV) conditions are ideal for experimental and theoretical study. In UHV, the intrinsic magnetic properties of these systems are protected from modification due to residual gas contamination and it is possible to use scanning tunneling microscopy (STM) to catalog the position and size specific to each particle.

In this work, we have successfully prepared Fe quantum dots on Cu(111) with the BLAG technique. Subsequent measurements show that the remanent magnetization (M_r) of the dot assembly is stable with respect to time at temperatures below 120 K. This stable magnetization and the well-defined transition temperature at which M_r vanishes clearly indicate ferromagnetic stability in the system. We have characterized our quantum dot assemblies with STM in order to simulate them

accurately in Monte Carlo calculations, which show that the dipolar interaction is the major driving force behind the ferromagnetic stability in the system.

Experiments were performed in UHV systems with base pressures below 10^{-10} Torr. The Cu(111) single crystal surface was prepared by cycles of 1 keV Ne ion sputtering and annealing to 800 K, before it was cooled to about 15 K. Inert Xe gas of 5N purity was then released into the UHV chamber. Typically, the sample was exposed to 200 L of Xe before Fe deposition. ($1 \text{ L} = 10^{-6} \text{ Torr-sec.}$) Iron was then evaporated from a thoroughly outgassed, high purity wire that was heated by electron bombardment. After the equivalent of 0.8 atomic layers of Fe was deposited, the sample was slowly warmed to 90 K to desorb the Xe buffer layer and allow the Fe dots to land on the Cu substrate. In-situ variable temperature STM and MOKE measurements were then performed.

STM studies indicate that this process results in the formation of Fe quantum dots on the Cu substrate that are shaped like flattened hemispheres. The average height of the quantum dots is 1.4 nm and the average width is 3.5 nm. The shape and size of the formed structures are surprisingly stable as the sample is allowed to warm from 90 K to room temperature. Figure 4.5 shows the STM morphology of the quantum dots at 90 K (a) and 298 K (b). The height distribution for the quantum dots is shown in Figure 5(c). This distribution is not appreciably different at low temperatures.

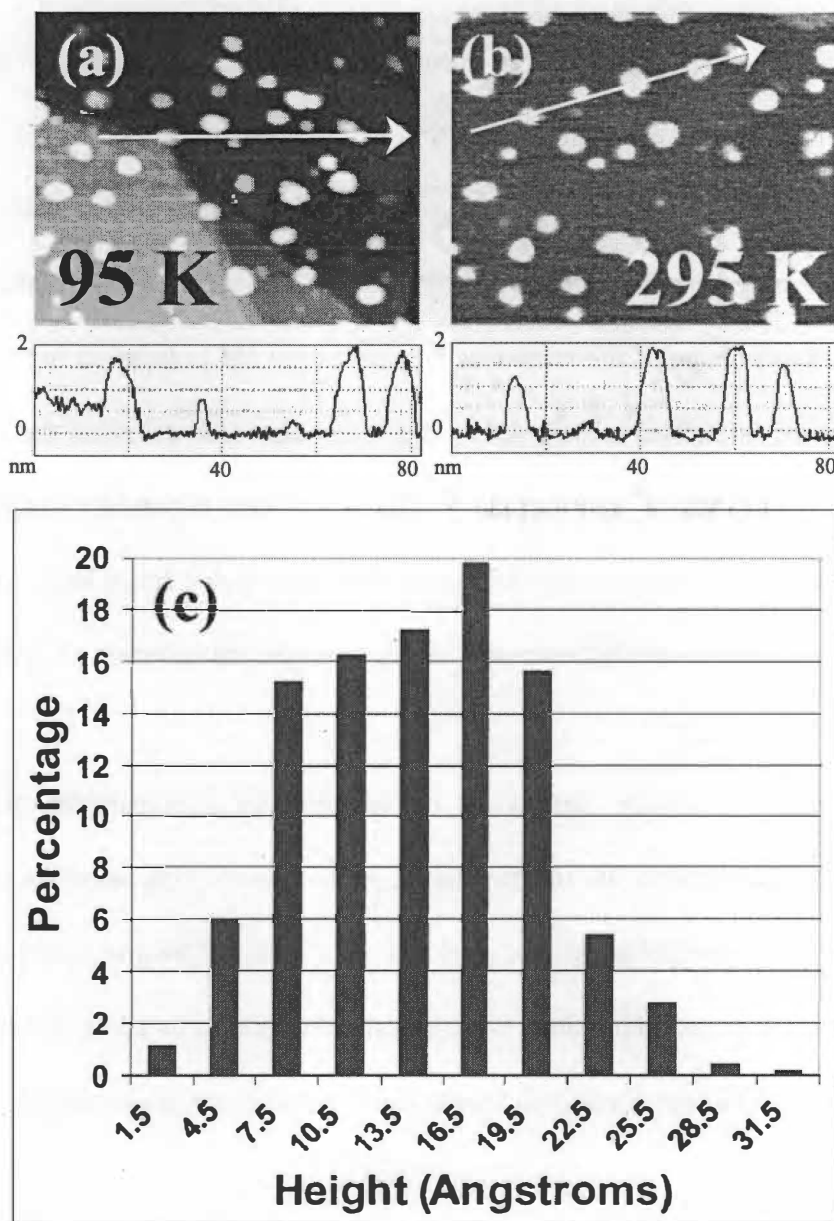


Figure 4.5: Morphology and thermal stability of Fe quantum dots on Cu(111). This data corresponds to a dot array made from 0.8 atomic layers of iron. The STM images in (a) and (b) show that the morphology of the dots does not change significantly as the temperature of the sample is raised from the growth temperature to 295 K. The histogram in (c) shows the height distribution of the dots. The histogram is based on a sample area which contained 685 individual Fe clusters.

4.2.2 Magnetic behavior of the quantum dots

MOKE magnetization curves were recorded with the magnetic field both perpendicular to and in the plane of the sample. Two of these curves are shown in Fig. 4.6. The hysteresis observed in the longitudinal configuration indicates that the easy axis of magnetization lies in the plane of the quantum dot array. The temperature dependence of the remanent magnetization (M_r) observed in the in-plane hysteresis loops is shown in Fig. 4.7. The remanence decreases as the sample is warmed, and vanishes at approximately 120 K. Time dependent magnetization measurements (see the inset in Fig. 4.7) show that M_r is stable for at least 30 seconds. This stability in time was characteristic of M_r over the entire range of temperatures studied.

The stable, non-zero remanence is indicative of inter-particle interactions. Without these interactions, the magnetization should decay exponentially with time, as predicted for superparamagnetic systems [7]. To determine whether or not particle-particle dipolar interactions were significant enough to allow the remanence to persist up to 120 K, we conducted Monte Carlo simulations of our samples.

4.2.3 Monte Carlo Simulations of Interacting Magnetic Nanoparticles

As described in our discussion of superparamagnetism in section 2.2, knowledge of the size distribution alone is sufficient for predicting the behavior of a system of non-interacting magnetic nanoparticles. This is not the case with assemblies

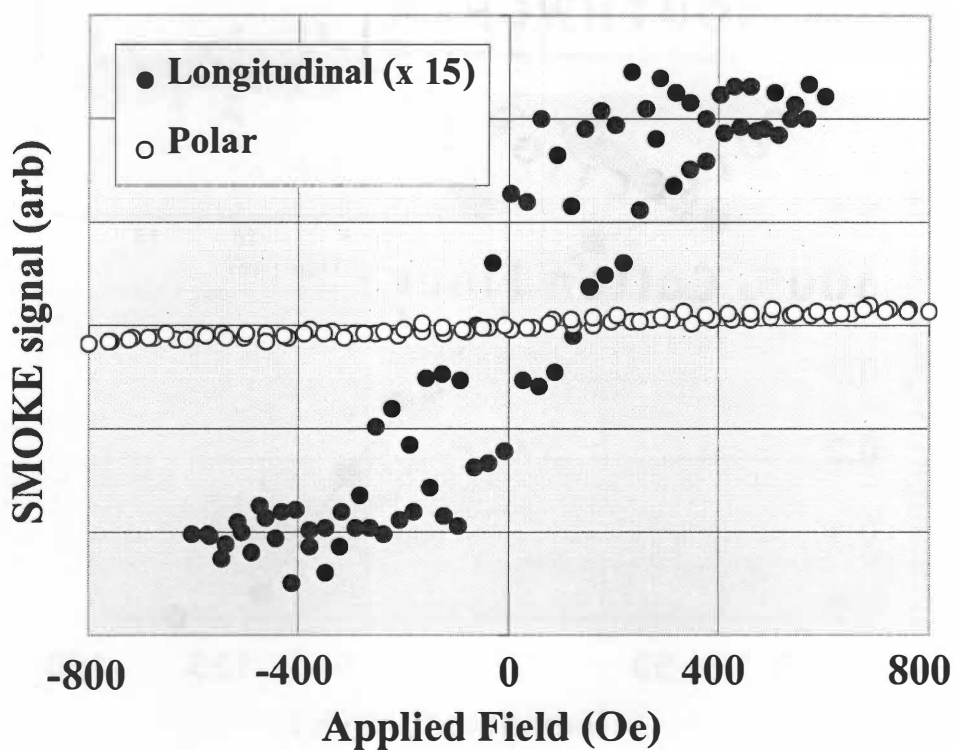


Figure 4.6: SMOKE magnetization curves for the Fe quantum dot assembly. The curves were recorded with the applied field perpendicular to the sample (polar MOKE) and in the plane of the sample (longitudinal MOKE). These data were taken at a sample temperature of 45 K.

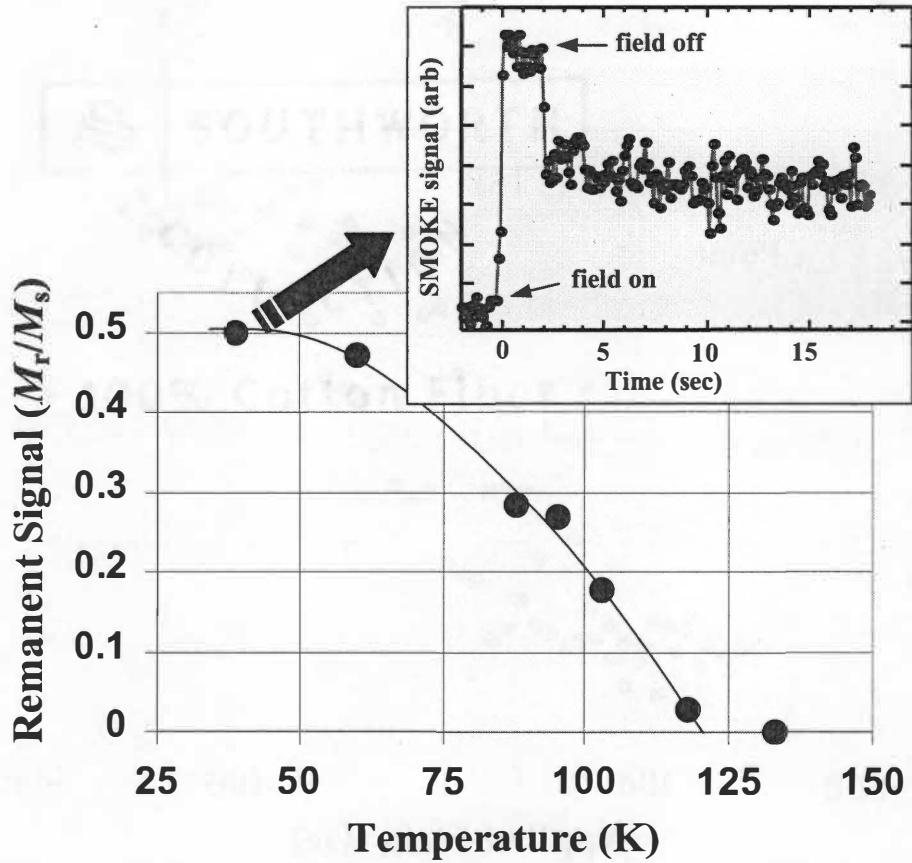


Figure 4.7: Time and temperature dependence of the dot magnetization. The lower plot shows the ratio of remanent (M_r) to saturation (M_s) as determined from hysteresis loops (as shown in Fig. 6) and time dependent measurements (as shown in the inset in this figure). The remanent magnetization is stable throughout this temperature range, and vanishes at approximately 120 K.

of particles that *do* interact with each other. Most interactions between objects, whether they are of a simple dipole nature, or of some more complicated, perhaps even substrate-mediated form, depend on the distance between the objects. Because of this, when interactions within a system of particles are being considered, the positions of the particles have to be known along with their sizes. This information is often difficult to obtain, and restricts our ability to build realistic and quantitative models of such systems.

In this sense, the present Fe quantum dot system lends itself very well to quantitative theoretical study. The system can be accurately simulated since the sizes and positions of each dot in a given area can be recorded with a scanning tunneling microscope (STM). In addition, the ultra-high vacuum environment in which the dots were grown and measured insures that the composition of the dots is well controlled. Unlike ultra-high vacuum experiments, in which repeating trials is time consuming and tedious, computer simulations can be easily rerun with different parameters, and are thus useful for developing our intuition about how these systems behave.

In order to examine the relative roles played by magneto-crystalline anisotropy and the dipolar interaction in the present Fe dot assemblies, Lee et al. [10] conducted Monte Carlo simulations that calculated the temperature dependence of the remanent magnetization. These simulations used the experimentally measured positions and sizes of the dots as input, which meant that dipole-dipole interactions between the dots could be calculated exactly, and were therefore not used as a fitting parameter. Each dot was modeled as a single dipole moment whose strength was determined by multiplying the bulk Fe magnetization (our SMOKE studies give

indirect evidence that the Fe dots are in a high-moment phase, for which this value for the magnetization is appropriate) by the experimentally determined dot volume. Each dot was then given a fixed uniaxial anisotropy axis (i.e. fixed easy axis of magnetization), whose orientation was randomly assigned.

The Hamiltonian for the system was given by

$$H = -\frac{1}{2} \sum_{i \neq j} \vec{m}_i \frac{3\hat{r}_{ij}\hat{r}_{ij} - 1}{|\vec{r}_{ij}|^3} \vec{m}_j + \sum_i 2|\vec{K}_i| \left(1 - (\hat{K}_i \cdot \hat{m}_i)^2\right)$$

In the first term, $\vec{m}_i$ is the magnetization of the i th particle, $\vec{r}_{ij}$ is a vector that points from the i th to the j th particle, and I is the identity matrix. This term is just the magnetostatic interaction energy between two dipoles, as in the first equation in section 2.2. In the second term, the vector $\vec{K}_i$ has a magnitude equal to $K_0 V_i$, where V_i is the volume of the i th dot and K_0 is an anisotropy constant that is the only fitting parameter in these simulations. The direction of $\vec{K}_i$ is along the randomly assigned direction of the fixed easy axis of magnetization for the i th dot. This term is simply the anisotropy energy. This can be seen by noting that if the angle between $\vec{K}_i$ and $\vec{m}_i$ is taken to be θ , then the contribution to the energy from the i th term is $K_0 V_i \sin^2(\theta)$, which is of the same form discussed when anisotropy constants were introduced in section 2.2.

In running the simulations, all moments were initially "saturated", or forced to point along a certain direction in the plane of the sample, and were then allowed to relax to their remanent state under the conditions of the Monte Carlo algorithm. On each pass, the Monte Carlo simulation chose a dot at random, altered the direction of

its magnetization, and calculated how that alteration changed the total energy of the system. If the total energy of the system was decreased by the move, the new state of the system was accepted. If the total energy was increased, then the new state was only accepted with a probability given by the Boltzmann factor $e^{-(\text{energy difference})/k_B T}$. This is the widely used "Metropolis" Monte Carlo algorithm [11].

The results of the simulations can be seen in Figs. 4.8 and 4.9. Figure 4.8 shows a snapshot of the simulated magnetization at 56 K for an array of Fe dots whose sizes and positions values have been obtained experimentally from STM images. Figure 9 shows both the measured and Monte Carlo simulated temperature dependence of remnant magnetization for a dot assembly made from 0.8 atomic layers of iron. The simulated data are in agreement with the measured values if the anisotropy constant K_0 is taken to be 6.58 times that of bulk bcc Fe. This difference will be discussed momentarily. Although the anisotropy energy plays the most important role in enabling a finite remnant magnetization and high critical temperature (~ 120 K), dipolar interactions also have a significant influence on the magnetic ordering. As shown in Fig. 4.9, with this optimized anisotropy constant, the Monte Carlo simulation indicated that the critical temperature would shift toward lower values (~ 100 K) if dipolar interactions were neglected. Figure 4.10 shows the time dependent behavior.

One might speculate that the large calculated magnetic anisotropy of 6.58 $K_{\text{Fe}}^{\text{bcc}}$ may be caused by the enhanced surface to volume ratio of the dots. Enhanced magnetic anisotropy of this magnitude has been often observed in ultrathin films, and tends to govern the direction of their easy axis of magnetization. Unlike the case at

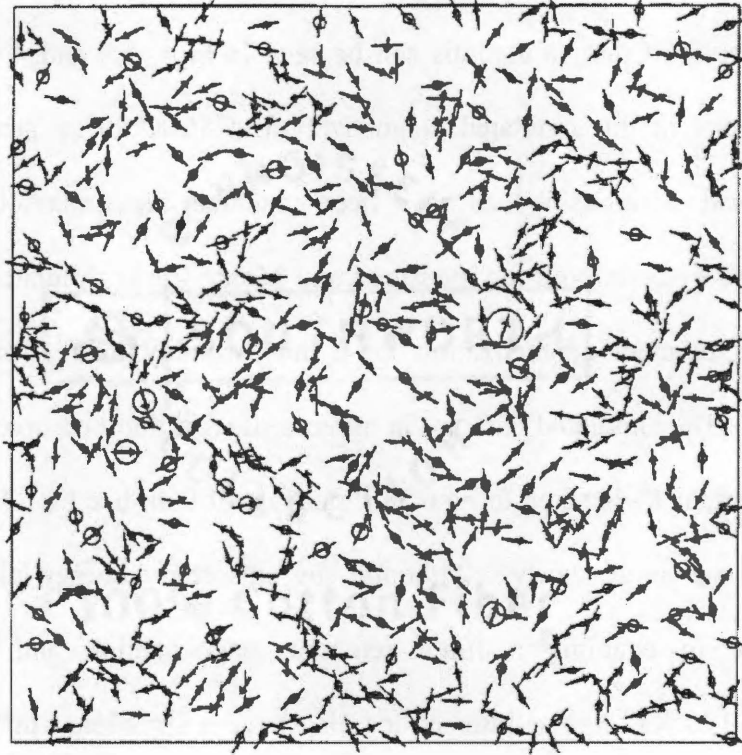


Figure 4.8: A snapshot of the magnetization of the magnetization of the dot assembly at 56 K, as generated by the Monte Carlo simulation. This figure contains 685 particles in a $240 \times 240 \text{ nm}^2$ area. The components of the magnetization are (0.482, -0.005, 0.001). The thin lines show the direction of the uniaxial anisotropy axes and the arrows indicate the projections of the particles' magnetization onto the XY plane. The sizes of the circles indicate the sizes of the particles. More details can be found in [10].

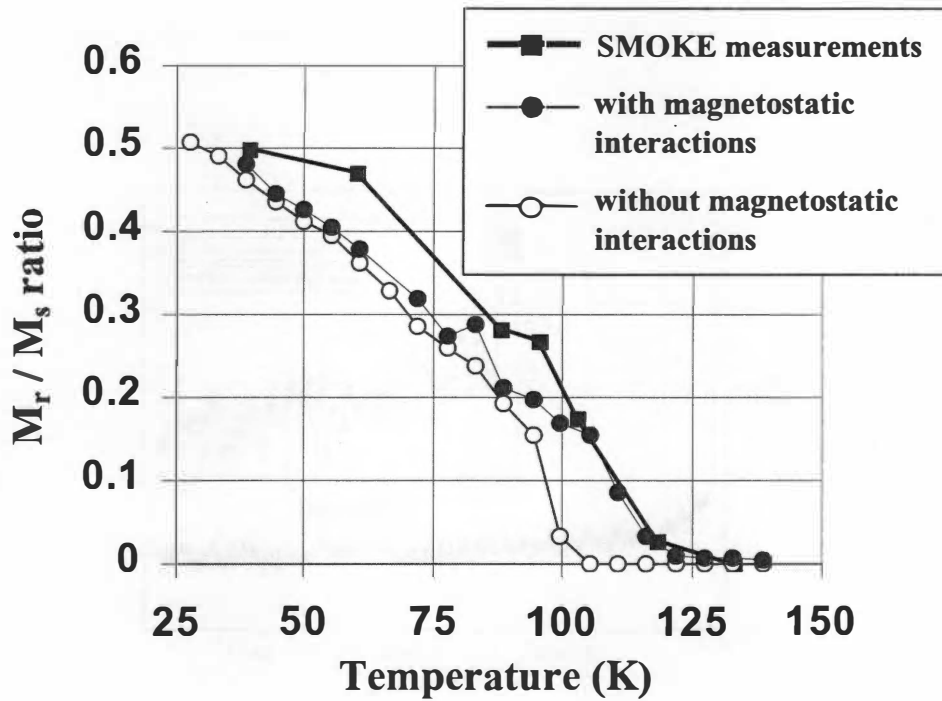


Figure 4.9: Monte Carlo fitting of the temperature dependence of the remanent magnetization of the quantum dot assemblies. The only adjustable parameter in the simulations, the anisotropy constant of the iron, was considered optimized when the Monte Carlo data (filled circles) fit the experimental data (filled squares) in the transition regime. Running the simulation *without* magnetostatic (dipolar) interactions between the dots shows the relative importance of the dipole interaction energy and anisotropy energy in this system.

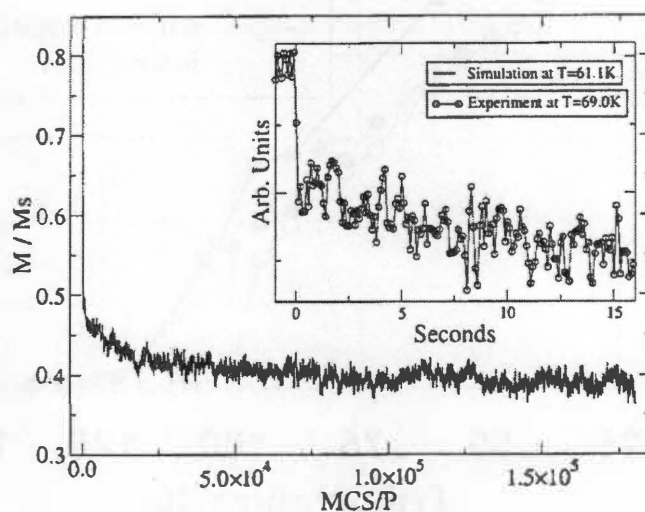


Figure 4.10: Time dependence of the remanent magnetization. Obtaining the amount of time that each Monte Carlo step represents is not straightforward. By comparing the time dependence of the remanence in a simulation (61.1 K) and an experiment (69 K), it can be estimated that 2×10^5 Monte Carlo steps per particle (MCS/P) corresponds to between 10 and 100 seconds.

the surface of an ultrathin film, the crystallographic orientation of surface atoms will vary from location to location on the dots, making analysis of the anisotropy very difficult. First principles calculations of single-layer-high step edge atoms have been performed, but, given the variety of possible lattice sites on a dot surface, calculations of their magnetic anisotropy are probably not feasible.

Despite the point made in the paragraph above, it actually is rather unexpected that the dots show such a large effective anisotropy. In ultra-thin films, the enhanced magneto-crystalline anisotropy that is often observed usually owes its existence to a distortion of the cubic unit cell that is brought about by the substrate. A high magnetocrystalline anisotropy in this system would indicate that substrate strongly influences atomic structure in this dot system as well. This possibility is surprising since the dots were not prepared directly on the substrate. In fact, the whole point of the buffer layer growth method was to *screen* the effects that the substrate has on Fe since these effects were detrimental to the production of nanostructures! The high value of the anisotropy constant perhaps even suggests that the influence of the substrate is strong enough to force the atomic structure of the dots to be face-centered cubic, as it is when iron is deposited directly on Cu(111). This, too, would be surprising since bcc is the natural low temperature phase for Fe and it is probably the atomic structure assumed by the Fe atoms as they form clusters on (or in) the xenon layer. We shall return to the question of the atomic structure of the dots in our concluding remarks in this Chapter.

4.2.4 Controlling the sizes and spacing of magnetic quantum dots

At present, it is not yet clear whether the actual anisotropy of the dot arrays really is enhanced relative to the bulk value. It is entirely possible that the anisotropy parameter obtained from the simulations is inflated simply because another important factor, like a dot-dot interaction that is not dipolar in nature, has been left out of the study. This could include an interaction similar to the “RKKY” interaction that is pictured in Fig. 1.4 back in Chapter 1. In this scenario, the magnetic moments of the dots interact with each other by inducing a polarization in the electrons of the non-magnetic substrate, just as is observed in magnetic/non-magnetic multi-layered structures.

In almost any physical system in which the nature of interactions between particles is unknown, it is vital to be able to vary the source and range of the interaction. For instance, fundamentals of electrostatic interactions were discovered through systematic control of the amount of charge on two objects (the sources) and of the distance between them (the range). In this quantum dot system, the nature of the behavior of these possible interactions could be uncovered by observing how the behavior of the system changes when the moments and spacing of the dots are varied. Since the magnetic moment of each dot depends on the number of atoms in the dot, learning how to systematically change the *sizes* and spacing of the dots becomes a crucial achievement.

We have systematically studied how two growth parameters can be used to tailor the sizes and spacing of the dots. These parameters were the amount of Fe

deposited and the thickness of the xenon buffer layer. Before we began, we expected the effect of increasing the Fe dose to be twofold. Additional iron atoms could either stick to existing dots, increasing the average cluster size, or could establish new nucleation sites, thereby increasing the number density of the dots on the Cu(111) surface. Increasing the Xe layer thickness was also expected to have two effects. If the buffer layer thickness was increased, Fe clusters would have more time to bump into each other as they worked their way toward the substrate. As the clusters merged together, the average dot size would increase, but the total number of dots would *decrease*. As the results in Fig. 4.11 show, this is indeed the case. What we did not guess was to what extent these two separate approaches would be useful in varying the size and spacing.

By comparing the vertical scales of plots (a) and (b) to plots (c) and (d) in Fig. 4.11, it becomes evident that changing the Xe buffer layer thickness gives the widest range in the dot sizes and spacing. At a fixed Xe exposure of 200 L, changing the amount of iron from 0.25 to 4.5 atomic layers caused the density of dots to increase by a factor of 2.5. At thicknesses larger than 4.5 ML, the buffer layer technique failed to produce isolated Fe clusters, but created a connected, or “percolated” network of clusters. At a fixed iron coverage of 1.05 ML, reducing the Xe exposure from 600 L to 10 L increased the dot density by a factor of 30. The large changes in density can be seen in the STM images in Fig. 4.12. In viewing these images, it is necessary to remember that the apparent widths of the dots cannot be compared due to differences in tip broadening effects in the images. Tip broadening is shown in Fig. 1.6 in Chapter 1.

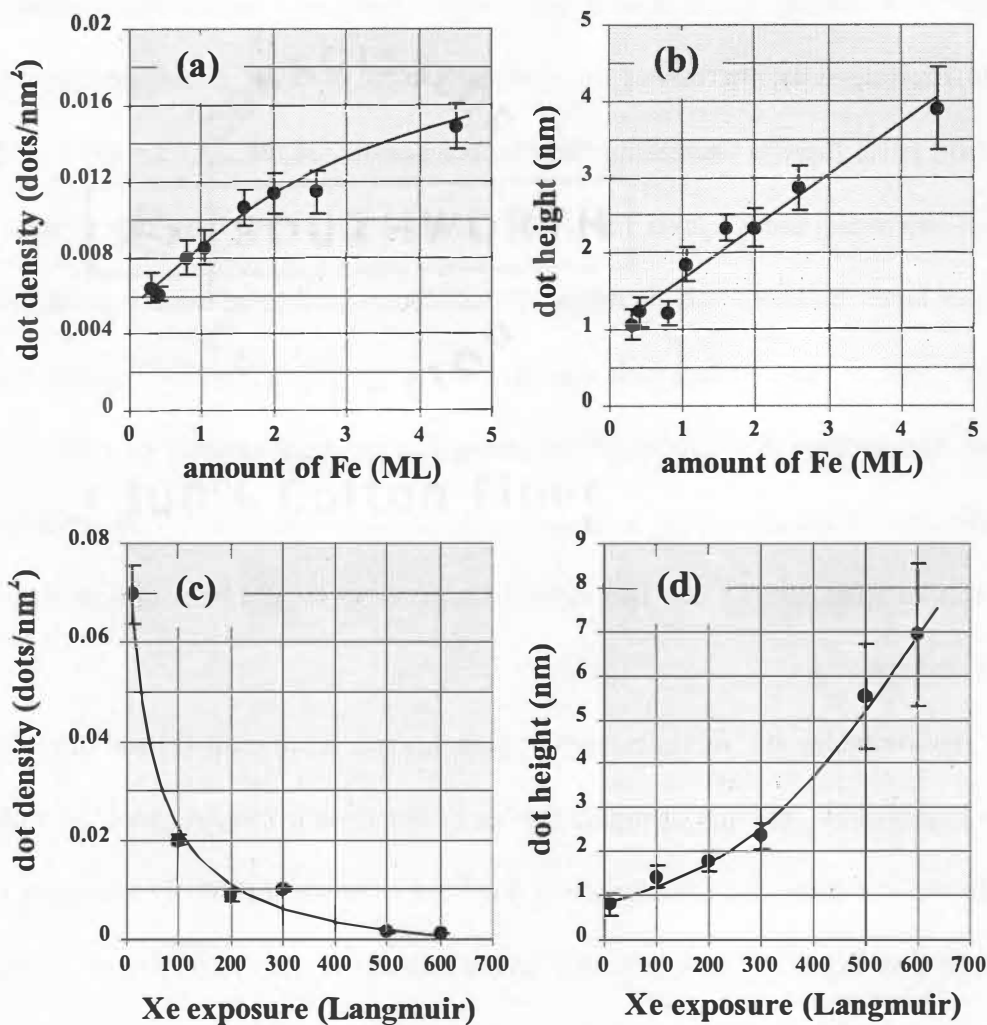


Figure 4.11: Controlling the size and spacing of the quantum dots. Plots (a) and (b), respectively, show that increasing the amount of deposited Fe when the xenon buffer layer thickness is fixed leads to an increase in the dot density and height. In these experiments, the Xe exposure was fixed at 200 L, where $1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{sec}$. In plots (c) and (d), the Fe dose was fixed at 1.05 ML and the Xe exposure (Xe layer thickness) was varied. Plot (c) shows that the dot density can be controlled over a wider range by varying the thickness of the Xe buffer layer. In (d) the dots are found to grow larger as the thickness of the buffer layer is increased. The error bars in the density plots were determined by taking the square root of the number of dots counted and dividing by the area considered. The width of each error bar in the height plots reflects the standard deviation of the mean of the height distribution that corresponds to each data point.

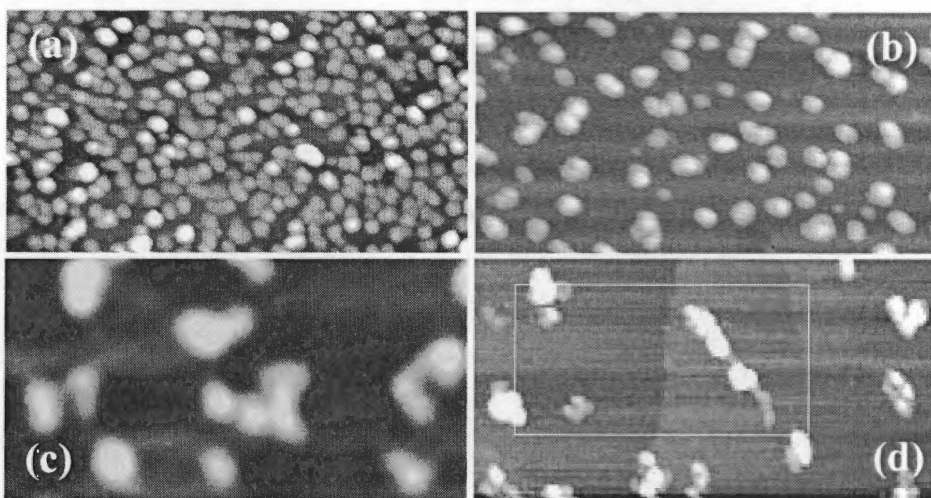


Figure 4.12: The effect of changing the buffer layer thickness. These STM images show the morphology that results when quantum dots are made from 1.05 ML Fe after following the buffer-layer-growth procedure with (a) 10 L, (b) 100 L, (c) 200 L, and (d) 500 L xenon exposures. Images (a), (b), (c), and the white box within image (d) depict $100 \times 50 \text{ nm}^2$ areas.

This ability to control the dot size and spacing should make it possible to confirm the validity of the anisotropy constant found in the Monte Carlo simulations. The SMOKE measurements and Monte Carlo simulations should be made for a series of samples in which the buffer layer thickness is systematically varied. Observing the sensitivity that the ordering temperature has on the dot spacing should make it readily possible to tell whether or not RKKY-like, inter-particle interactions play an important role in stabilizing magnetic order in the system. These additional magnetic and Monte Carlo studies have not yet been performed at the time of this writing.

4.3 Direct observation of the effect of dimensional confinement on magnetism

Our success in producing and characterizing isolated Fe quantum dots on the Cu(111) surface provides one piece of an important puzzle in this field. When combined with the results from our collaborators in Halle, Germany, our studies provide a more complete view, unconvoluted by the effects of changing templates, of how nanostructuring affects the magnetic properties of a material. In this section, we will discuss how forcing a magnetic material to grow as a flat film, wire array, and dot assembly affects its magnetic properties. We begin by showing how the Halle group was able to produce atomically flat films and nanowire arrays from Fe/Cu(111). We will then present experimental results that show how the behavior of a fixed amount of Fe changes when it is grown as a film, wires array, and quantum dot assembly on the Cu(111) surface.

4.3.1 Synthesis of 2D ultra-thin films and 1D nanowire arrays of Fe on Cu(111)

In order to overcome the challenge of producing atomically flat iron films on this surface, the Halle group employed a growth technique called laser molecular beam epitaxy (MBE). The technique, and an example of the smooth Fe/Cu(111) films that it can produce are shown in Fig. 4.13. Laser MBE incorporates many of the details of its parent technique, pulsed laser deposition (PLD). In PLD, a powerful, nanosecond-pulsed Excimer laser is focused onto a target. After a complex interaction between the light pulse and the solid [12], a plasma plume is ejected from the target and expands quickly toward a substrate placed nearby. The plasma plume consists mainly of neutral atoms from the target that have a relatively moderate energy (~ 1 eV) plus a small fraction of ions whose energy can be as high as 100 eV. A remarkable feature of PLD is that it yields an instantaneous deposition rate (during each laser pulse) that is on the order of 10^6 ML/minute or higher, which is six orders of magnitude higher than that of thermal MBE. This high flux of atoms, according to growth theory [13-15], tends to enhance the nucleation density, or number of sites per unit area at which deposited atoms will seed island growth on the substrate. This, in turn, tends to produce a smoother film than would be observed if the nucleation density was lower.

The STM image in Fig. 4.13 shows that nearly ideal layer-by-layer growth of fcc Fe films can be achieved with the help of laser MBE growth. This is in stark contrast to the multi-layer island morphology of Fe/Cu(111) produced with thermal MBE. The surface morphologies of single atomic layers of Fe/Cu(111) grown by

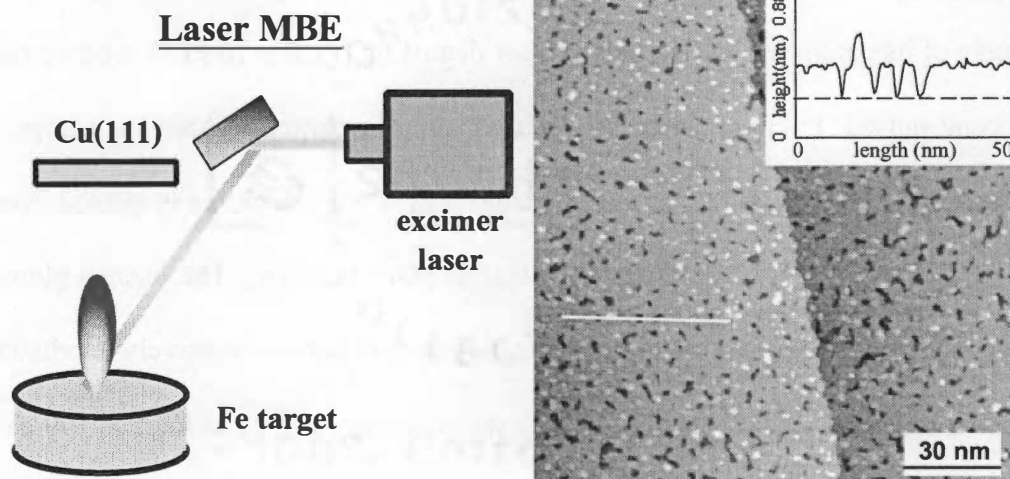


Figure 4.13: Growth technique for atomically flat films of Fe/Cu(111). In laser MBE, high intensity light pulses are sent toward a target where they ablate the target material. The plume of ejected target material is directed toward a nearby substrate. The key feature of this technique is that during each laser pulse, the number of atoms incident on the substrate is higher than is found in conventional MBE by a factor of 10^6 . This results in a high density of nucleation sites for the resulting film, which is found to be nearly atomically smooth

laser MBE and thermal MBE are compared in Fig. 4.14. Both films were prepared at an identical substrate temperature of 220 K. The thermal MBE film, as discussed earlier, exhibits typical multi-layer island morphology that leaves a considerable fraction of the Cu surface uncovered. The laser MBE Fe film, at a nominal thickness of one complete monolayer, covers about 95% of the substrate, which is nearly a perfect film. The Halle group found that this two-dimensional layer-by-layer growth persists until the film thickness reaches 6 ML and an fcc-bcc structural transition occurs [16].

Most systems that show one-dimensional stripe growth do so via the common phenomenon called step-flow growth. This is the process by which our FeCo alloy nanowires and the single- and double-layer stripes of Fe that we showed in Fig. 1.9 in Chapter 1 were formed on the W(110) surface. In those systems, the substrate was annealed to a few hundred degrees above room temperature either during or after the overlayer atoms were deposited. At the elevated temperature, the added atoms step-flowed, or migrated on an atomic terrace of the substrate until they came to rest along the vertical wall created by the substrate atoms of the next terrace. For this to occur in these systems, the adatoms had to have a strong tendency to or spread out on the substrate rather than balling up into clusters and had to strongly oppose intermixing with the substrate atoms at the annealing temperature. As we described in Chapter 3, that, in turn, required that the substrate had a considerably higher surface free energy than that of the deposited material.

That criterion is not met in the Fe/Cu(111) system since the surface free energy of Fe is considerably higher than that of Cu [17]. Luckily, and perhaps oddly

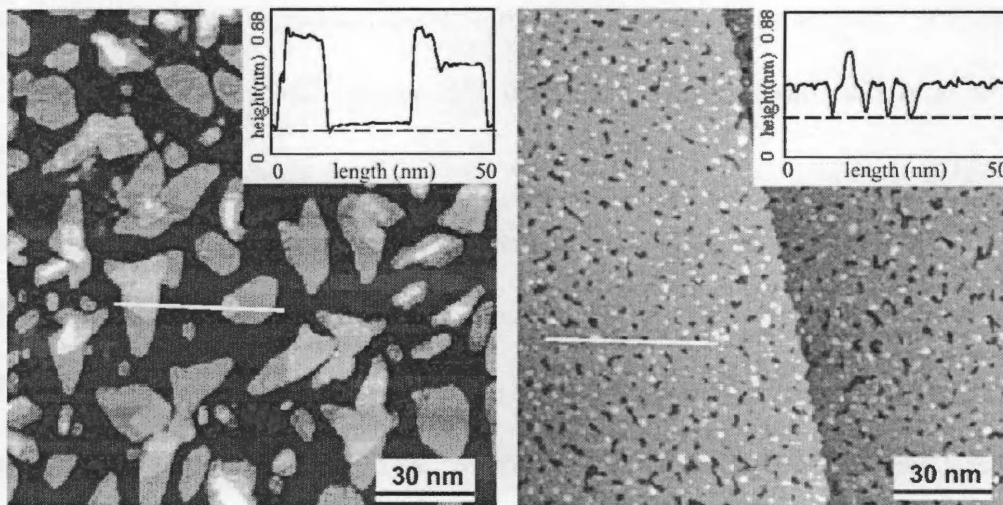


Figure 4.14: Comparison of single atomic layers of Fe/Cu(111) grown by thermal MBE and laser MBE [3]. The STM image on the left shows the multilayer island morphology that results when 1.0 ML Fe is deposited on Cu(111) with thermal MBE. The STM image on the right shows the 95% perfect monolayer that can be formed via pulsed laser deposition.

as well, Fe adatoms in this particular system have a strong preference to nucleate at the *top* edges of the substrate steps, rather than in the kink at the bottom of the steps! This occurs at room temperature or even slightly below. To exploit this step decoration effect, the Halle group chose a Cu(111) substrate which was miscut relative to the (111) plane by 1.2 degrees. This produced a surface of parallel Cu(111) terraces whose edges were separated by approximately 10 nm. This step density was high enough to allow almost all Fe adatoms to nucleate at step edge sites. Figure 4.15 shows STM images taken from several of these Fe/Cu(111) stripe arrays with various nominal thicknesses. Depending on the thickness, the stripes were 1 to 2 ML high and 2 to 5 nm wide. Although step decoration is an unusual phenomenon, it is not limited to the Fe/Cu(111) system. Later, in Chapter 5, we will show how this step decoration effect can also be used to fabricate Fe nanowires on an insulating NaCl(100) substrate.

A morphological comparison of the 2D, 1D, and 0D manifestations of Fe on Cu(111) can be made by looking at the room temperature (300 ± 5 K) STM images in Fig. 4.3. The Fe film consists of monolayer high islands that just reach the percolation threshold, which is the point at which the film becomes connected to itself throughout its entirety. The Fe stripes are parallel and aligned along the substrate $\langle 110 \rangle$ direction. They are typically between 2 and 5 nm wide and are 0.2 to 0.4 nm high. The average center-to-center distance between them is about 10 nm, in accordance with the average nearest-neighbor step separation of the miscut Cu(111) template. The Fe dots, as we discussed in Sec. 4.2.1, are nearly hemispherical in shape, with an average height of 1.4 nm.

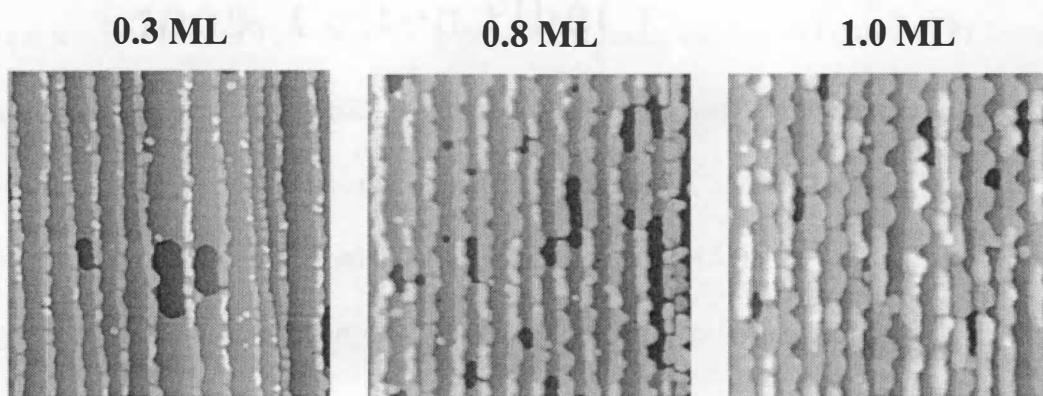


Figure 4.15: Synthesis of Fe nanostripes on Cu(111) via step edge decoration [3,6]. Each of the STM images above corresponds to a $100 \times 100 \text{ nm}^2$ area. By varying the amount of Fe dosed, Shen *et al.* were able to vary the width and spacing of the stripes.

4.3.2 Direct comparison of films, wire arrays, and dot assemblies made from 80% of an atomic layer of Fe

Direct comparison of the magnetic properties of the film, stripes, and dots of Fe yields surprising results. In Fig. 4.16 we show SMOKE magnetization curves that were recorded at 45 K for each of the three nanostructures. The first difference that we note among the three structures lies in their anisotropies. The workers in Halle found that for the ultrathin film and nanowire array, the easy axis of magnetization was perpendicular to the sample surface. As we discussed in Sec. 4.2.2, no magnetic response could be observed in the polar geometry, even though the Kerr response is an order of magnitude larger in that configuration (see Sec. 2.4.4) and would be easy to observe if perpendicular magnetization were present. The curve corresponding to the dots that we show in Fig. 4.16 was observed in the longitudinal geometry, indicating that the easy axis definitely lies in the plane of the sample.

Given the fact that the 0.8-ML film and 0.8-ML wire array show perpendicular anisotropy, it is mysterious that the dots show such a preference for in-plane magnetization. Shape, or dipolar anisotropy usually favors in-plane magnetization in film systems, but this effect cannot be the main factor here. Flat films whose thicknesses (d) are on the order of the average height of these quantum dots (10 atomic layers) typically show in-plane magnetization due to the fact the dipolar anisotropy energy ($2\pi M^2 d$) term is large enough to outweigh other anisotropies. Dipolar anisotropy typically controls the magnetization at such “large” film thicknesses. The fact that these dots are much thicker than the 0.8-ML film,

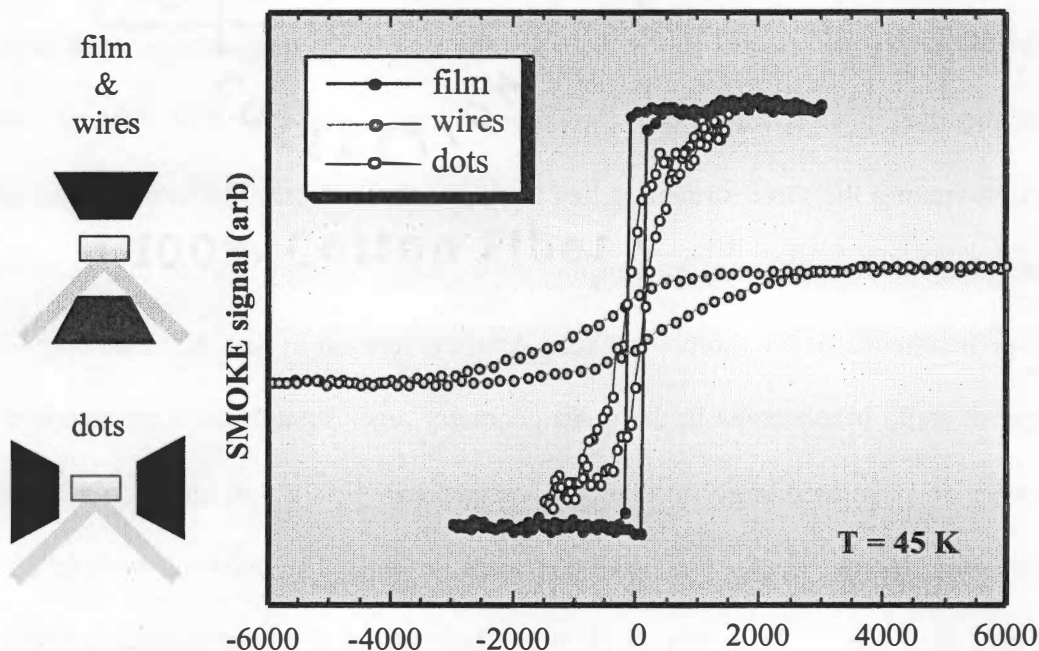


Figure 4.16: Magnetization curves and anisotropy for 2D, 1D, and 0D manifestations of iron on Cu(111). The easy axes of the films and wires were found to be perpendicular to the plane of the sample surface (polar Kerr effect), as indicated in the schematic at the upper left. The dots exhibit an in-plane easy axis (longitudinal Kerr effect). Since the magnetization of the nanowire system is time-dependent, the shape of its hysteresis loop in the plot on the right depends greatly on the amount of time required to sweep the field when taking the scan. The heights of the hysteresis loops are normalized as described in the text, indicating that the moment per atom in the dot system is equal to that observed in ultrathin films. The moment per atom is reduced considerably in the nanowire system.

however, does not mean that they should experience a larger in-plane anisotropy due to dipolar effects. In these dots, the width to height ratio is much smaller than of that of the films. This means that the demagnetizing field within the dots should be smaller than it is in films, and, as we discussed in Chapter 2, the demagnetizing field determines the dipolar (shape) anisotropy. For this reason, shape anisotropy should play less of a role in the dots than it does in films.

SMOKE is not a particularly good technique for measuring actual values for atomic moment. SQUID is a much more reliable technique for this purpose. The fact that the magneto-optical effects that it measures are directly proportional to the total moment of the sample however, makes it possible to make a good estimate of the average moment per atom by comparing the signal obtained from an unknown sample to that of a sample with a known atomic moment. This direct proportionality is difficult to prove theoretically for quantum dot and nanowire samples, but the plot in Fig. 4.17 is just one example of many that this is *experimentally* the case. To make the polar and longitudinal Kerr signals comparable, they were normalized by the SMOKE intensities that were observed when measuring thick bcc Fe films (> 4 ML) on Cu(111) in both geometries. Because the thick bcc Fe/Cu(111) films are known to have a magnetic moment of $2.2\mu_B$, this normalization allows us to compare the magnetic moments of the three different Fe nanostructures. The plot in Fig. 4.17 reveals that the magnetic moment of the film and the dot assembly is similar to that of bulk bcc Fe ($2.2\mu_B$), whereas the moment of the stripes is considerably reduced ($0.5\mu_B$).

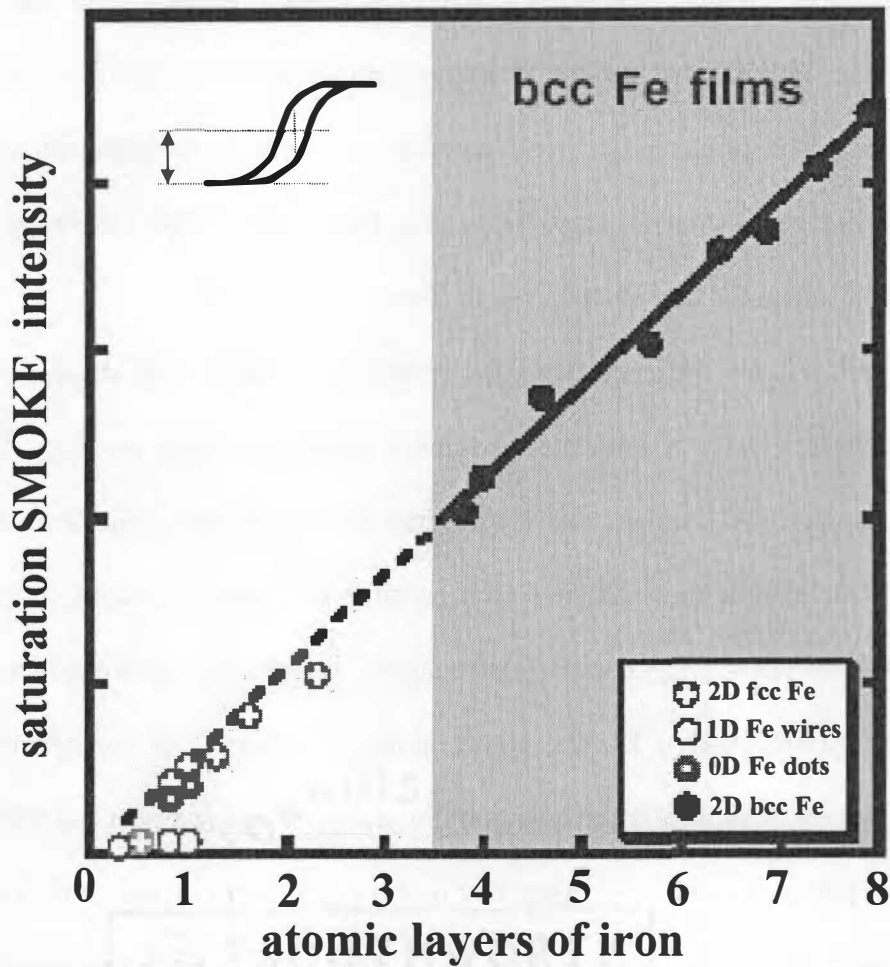


Figure 4.17: Determining magnetic moments from the thickness dependence of Kerr intensities. Here, the saturation SMOKE intensity (which is half of the height of measured magnetization curves, as shown in the drawing at the upper left) is plotted against the amount of Fe deposited on Cu(111). Thick bcc films are known to have an atomic moment equal to 2.2 bohr magnetons, which is the atomic moment of bulk iron. The linear dependence of this plot for data corresponding to bcc Fe films simply illustrates the linear dependence of Kerr intensity on the total moment of the sample as more atoms are added. Data points for laser-MBE-grown fcc Fe/Cu(111) films and buffer-layer grown quantum dots fall on the line established by the bcc Fe measurements, indicating that they have a similar atomic moment. The data corresponding to the one-dimensional nanostripes fall well below this line, indicating a much lower moment per atom for this manifestation of iron on Cu(111).

We caution the reader that the facts that the data for the dot saturation signal falls on the line that corresponds to $2.2 \mu_B$ in Fig. 4.17 and that the data for the saturation intensity for the wires is reduced by a factor of $0.5/2.2$ is *not* sufficient to support a bold claim that $2.2 \mu_B$ and $0.5 \mu_B$ are the exact atomic moments for the dot and nanostripe structures. When a material is arranged in dot and nanostripe forms, the elements of the dielectric and conductivity tensors that determine their Kerr responses are likely to be changed compared to those of a flat film. However, measurements made with x-ray magnetic circular dichroism (XMCD), a technique that can be used to directly determine the atomic moment, have shown that the per-atom moment in the stripes is $0.7 \pm 0.2 \mu_B$. This is in excellent agreement with the estimate obtained from the SMOKE intensities in Fig. 4.17.

Along with the magnetic moment, the stability of magnetic order with respect to time and temperature is also expected to be strongly dependent on spatial confinement. Measurements of the time-dependence of the magnetization of the three manifestations of 0.8 ML Fe/Cu(111) are shown in Fig. 4.18. The curves were all recorded at 45 K and were all initiated after the magnet was taken through a degaussing routine with the sample between the pole pieces. After this, we recorded the Kerr intensity for several seconds with the system in this demagnetized state to establish a baseline signal level. This is the horizontal segment of data that appears on the left side of the time origin ($t = 0$) of each plot in the figure. At $t = 0$, a current pulse was sent through the magnet so as to establish a field that would saturate the magnetic moments of the nanostructures along their respective easy axes. This explains the jump in Kerr intensity can be seen at $t = 0$. After a few seconds (ten in

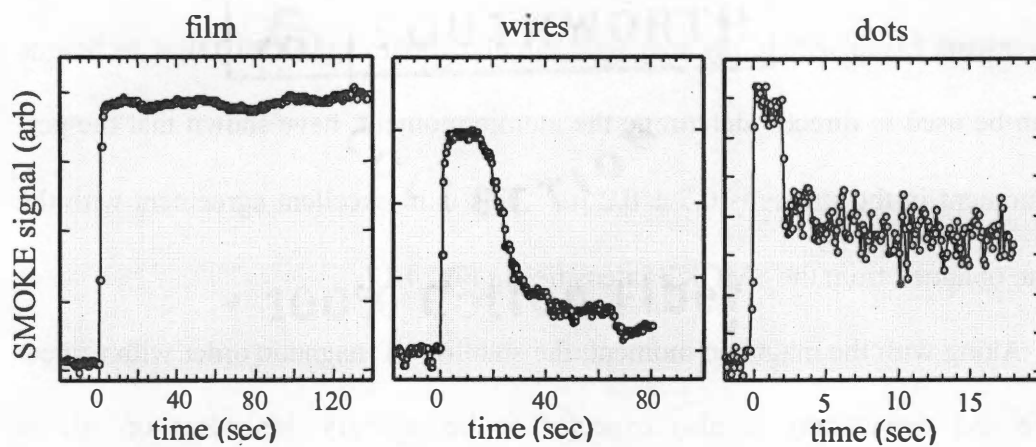


Figure 4.18: Time dependence of the remanent magnetization for films, wires, and dots of Fe on Cu(111).

the case of the films and wires, and two in the case of the dots) the field was abruptly removed and we continued to monitor the Kerr intensity.

The magnetization of the film remained constant when the field was removed, in agreement with what was implied by the sharp, rectangular hysteresis loop in the previous figure. This is a signature of a ferromagnetic system whose moments have been aligned along an easy axis. The magnetization (M) of the wire array melted away with time with a decay constant a bit less than 40 seconds, as one would find in a superparamagnetic system ($M = M_0 e^{-t/\tau}$) that wasn't far above its blocking temperature. The figure shows that after a sharp, initial decay, the remanent magnetization of the dots is quite stable with respect to time.

The effect of temperature on the remanent magnetization is shown in Fig 4.19. Both the Fe film and the Fe dot assembly exhibit well-defined ordering temperatures of about 100 K and 110 K, respectively. Above these temperatures, the Fe films become paramagnetic, while the Fe dot assembly is superparamagnetic, with each individual dot preserving its magnetic moment. That the individual dots retain their moment is evidenced by the observation of a non-zero saturation magnetization at a modest field (~ 600 Oe) at temperatures (up to 300 K) that were well above the temperature at which the remanence vanished. The Fe stripes seem to be above any well-defined ordering/blocking temperature in the temperature regime in which they were studied, because their remanence depends greatly on the duration of the measurement.

Before making concluding remarks, we note that we may have failed to produce 2D, 1D, and "0D" manifestations of the same magnetic material in one sense.

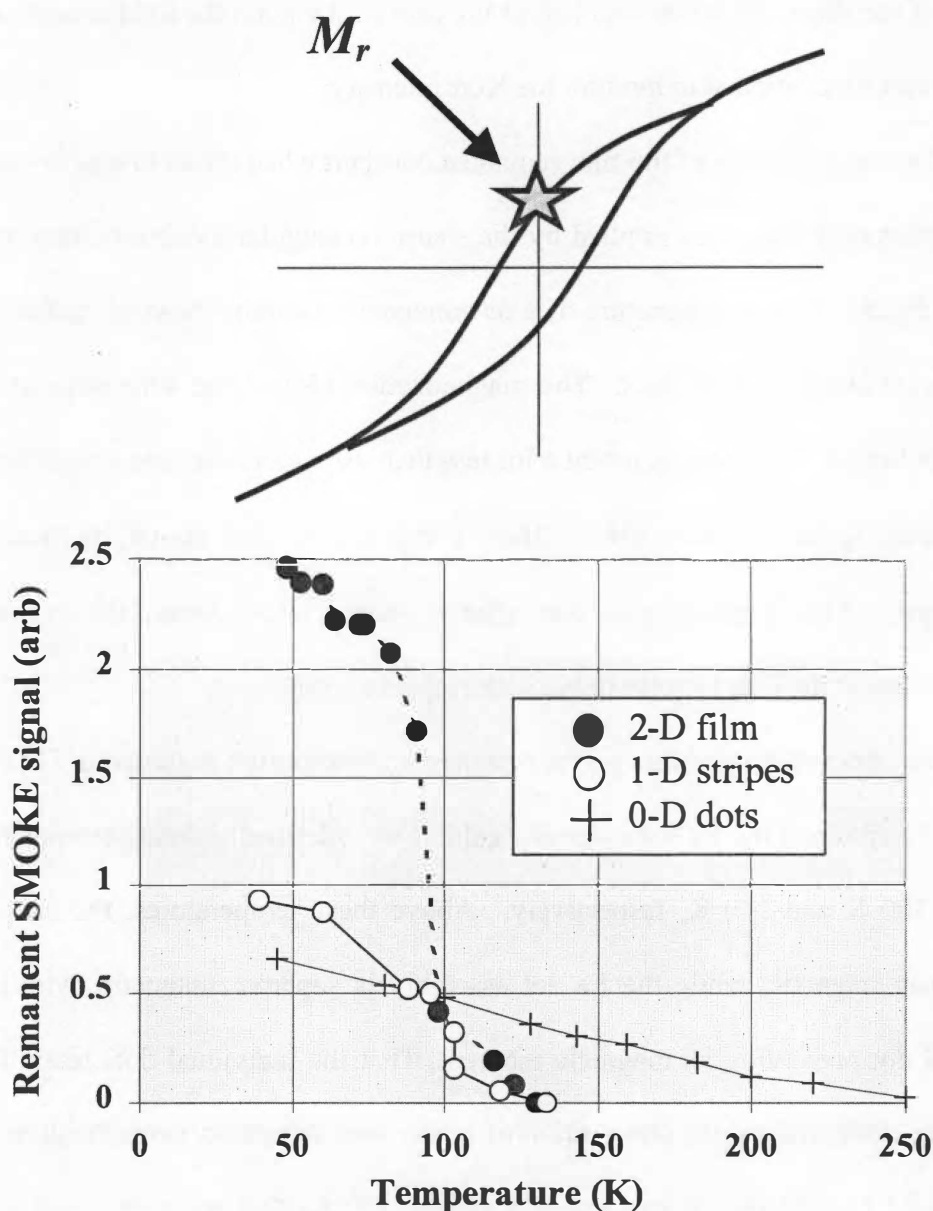


Figure 4.19: Temperature dependence of the remanent magnetization in nanostructures made from 0.8 ML Fe on Cu(111). The film and dots show similar Curie temperatures of 100 ± 10 K and 110 ± 10 K, respectively. Since the value of the remanent magnetization of the wires is strongly time-dependent, as shown in the previous figure, they do not have a well-defined magnetic transition temperature (or at least not one in this range). The data shown here were taken from hysteresis loops which each took approximately two minutes to acquire. Changing the duration of the data acquisition would not affect the curves for the ultrathin film and quantum dots, but would change the shape of the curve that corresponds to the nanowire arrays.

We know that the atomic structure of the 2D films and 1D nanowires copies the fcc structure of the Cu(111) substrate. The conclusions that we can draw about the effect the effect of reducing the dimensionality of the system from two and one dimensions to “zero” are limited by the fact that the atomic structure of the quantum dots remains unknown.

When the dots begin to form on the xenon layer, one would guess that the lattice structure of the Fe atoms is most likely to be body-centered cubic (bcc) since that is the crystal structure in which Fe is most often found. Unlike the bare Cu surface, the Xe atoms most likely do not strain the Fe clusters in such a way that an unusual iron structure forms. What happens when the dots land on the Cu substrate? Do they remain bcc, or does the copper surface force them to become fcc? Clearly, there is some interaction between the substrate and the dots because the dots are not easily dislodged by the probe microscope tip (this was never observed) and the dots collect in rows at terrace edges. Thirdly, the flattened shape of the dots also suggests a interaction with the substrate and may indicate that they could develop an epitaxial relationship or atomic registry with the Cu(111) lattice as they relax or “sag” on the surface. This, however, is pure speculation since the shape and size of the dots before the Xe is sublimated is completely unknown.

We attempted to measure the atomic arrangement with glancing-angle x-ray diffraction at the Advanced Photon Source (APS) synchrotron at Argonne National Laboratory. No evidence for bcc structure in the dots was observed, but this result is inconclusive for at least two reasons. The first problem with this approach was that the dot assemblies could not be prepared in the chamber at the end of the beamline at

Argonne. This meant that they had to be prepared at ORNL and then capped with a protective Cu layer to keep them from oxidizing when they were removed from ultrahigh vacuum. The additional Cu could have modified the atomic structure of the dots. The second problem is that even if the dots were bcc, their crystal axes could have been randomly oriented relative to each other. This would have diffused the bcc diffraction peak intensity into rings, which would have been too faint to observe since the diffraction was resulting from such a tiny amount of material. Our collaborators' attempts to determine the crystal structure of the dots with transmission electron microscopy (TEM) were also inconclusive.

As we pointed out in Sec. 1.3, textbook statistical models predict that long-range ferromagnetic order should become less and less stable as the dimensionality of a system is reduced. This tendency does not hold as we change the arrangement of 80% of an atomic layer of Fe from the form of nanowires to that of isolated quantum dots.

The model of superparamagnetic systems that we presented in Chapter 2 tells us that the magnetization of these systems should decay by a factor proportional to $e^{KV/k_B T}$. Since the volume of the individual dots is smaller than that of the spin blocks in the wire system [18], it is surprising that the dot assembly shows such an increased stability.

The non-monotonic response of the magnetic properties to the number of dimensions of spatial confinement is likely a direct consequence of the abnormally strong interplay between atomic structure and magnetism in the fcc Fe system. We discussed the strong dependence of the magnetic properties on the volume of the fcc

unit cell in the first section of Chapter 3. In forming ultrathin films, stripe arrays, and dot assemblies on Cu(111), the Fe is likely to assume slightly varying lattice constants. This is because the number of step-edge and surface atoms, which provide channels for relieving strain from the structures, is different for films, wires, and dots. This means that the strain that the Cu substrate, with its slightly mismatched lattice constant, imparts to the nanostructures would be different in each case.

In this first attempt to isolate the effects of nanostructuring on the properties of a magnetic material, we have found that the anisotropy, ordering temperature, and time-dependent behavior do not change monotonically or predictably as the structures are further confined. These have been the results for just one system; namely Fe on the Cu(111) surface. These systematic studies need to be extended to other overlayer/substrate systems to continue to build our intuition about the effects of nanostructuring. The beauty of the approach that we've taken here is that the techniques that were used are by no means only effective for the Fe/Cu(111) system. The approach can certainly be applied to other materials, under the condition that they show step-flow or step-edge decoration in order to assist the formation of nanowires. Iron and cobalt on the W(110) surface would be excellent candidates.

Chapter 5

New Directions

5.1 Transport in magnetic nanowires

5.1.1 Introduction

Each of the experiments that we discussed in the last two chapters is an example of progress in a new direction of study that could be followed to develop our understanding of how to tailor the behavior of magnetic nanostructures. First, we presented our work on controlling magnetic anisotropy in ultrathin films. We found a completely new mechanism for inducing a spin-flop transition in a magnetic film and a general method by which capping atoms could be used to teach us about the competing factors that determine the film's easy axis. Second, we explored how magnetic ordering in a nanostripe system could be tailored by changing its composition. Thirdly, we have found a way to study the relative importance of inter-particle interactions and properties inherent to isolated particles in magnetic dot assemblies. Finally, and perhaps most significantly, we have found a general approach by which all three types of nanostructures (films, stripes, and isolated clusters) can be fabricated from the same amount of the same material on the same substrate. This made it possible to observe how the magnitude and the time-,

temperature-, and directional-dependence of the magnetization of a material are modified as it is systematically confined in space.

Because of the metal-on-metal nature of the systems that we have discussed so far (namely $\text{Fe}_{1-x}\text{Co}_x/\text{W}(110)$ [1], $\text{Fe}/\text{Cu}(100)$ [2-4], and $\text{Fe}/\text{Cu}(111)$ [5]) we have neglected one important aspect of low-dimensional magnetic systems. The main reason that the study of magnetic nanostructures has become a hot area in condensed-matter physics is because of their *transport* properties. It is through electron transport that a nanoscopic phenomenon can be made to show itself in a macroscopically observable, useful way. It is for this reason that the next decade will see a flurry of activity in magnetic nanostructures prepared on insulating or semiconducting surfaces, or perhaps free-standing nanostructures, when possible.

5.1.2 Metal-on-insulator systems and free-standing nanostructures

One could rightfully argue that the magnetic nanowires that we discussed in the last chapter were not truly *wires* at all since they were prepared on a conducting, metallic, tungsten template. Likewise, the electrons in the 2-D, 1-D, and “0-D” structures that were described were not truly confined since the $\text{Cu}(111)$ substrate on which they were prepared is an excellent conductor. In this chapter we will focus on the synthesis and magnetic properties of Fe nanostructures on the insulating $\text{NaCl}(100)$ surface. Magnetic metal-on-insulator systems like this are a promising new frontier since they open the possibility of looking at magnetic field dependent *transport* in magnetic nanostructures.

The invention of the transistor and the development of the GMR spin-valve are two of the most monumental achievements in condensed-matter physics. In both of these devices, an external parameter that is easy to control can be used to establish whether or not a current can be easily sent through them. In the case of a transistor, it is the voltage. In a spin-valve, it's the orientation of the magnetization of the magnetic layers. What would happen if we could pass current through a single magnetic nanowire? Would we see, for instance, drastic changes in the current that we could pass through the wire as we modified the number and proximity of domain walls in the wire? After advances in the synthesizing nanowires on an insulating substrate have been made, one can envision probing the relationship between conductivity and domains or field-dependent conductivity in single wires via the method shown in Fig. 5.1.

As we have often found to be the case in working with magnetic nanostructures, synthesis is a primary challenge. Chemical means have led to a great deal of progress in the study of transport in magnetic nanowires. One particularly powerful and popular technique has been electroplating [6-10] or "electroless deposition" [10] of magnetic metal atoms from solution into the parallel, cylindrical pores of special insulating media. In this way, parallel arrays of nanowires with diameters down to ~ 30 nm have been synthesized. The most common method for establishing an electrical connection to a single nanowire is shown in Fig. 5.2. While the wires are being electroplated, they grow upward from the bottom anode. When the first wire contacts the top metallic layer, a sharp increase in plating current is observed due to the sudden, sharp increase in the surface area of the anode. The

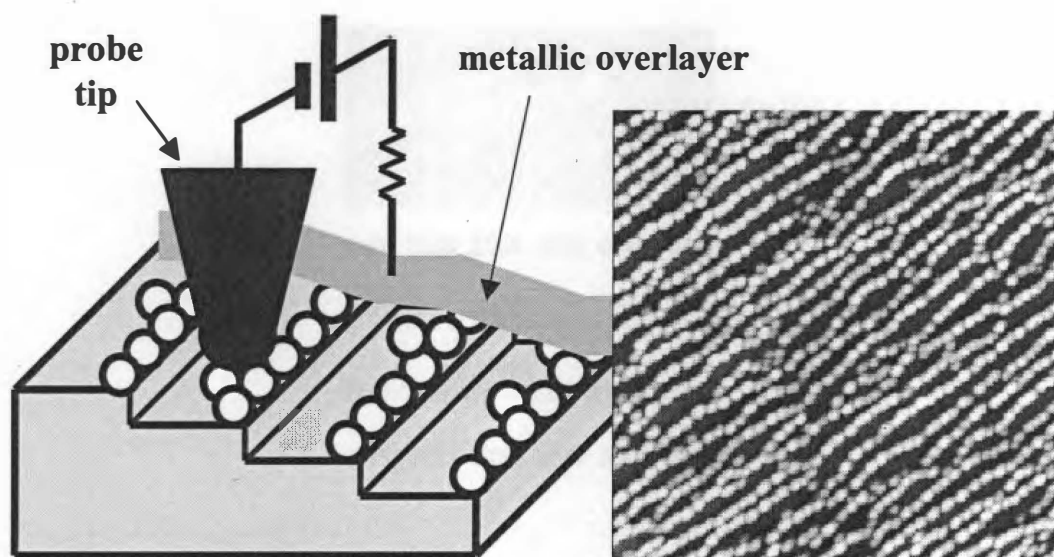


Figure 5.1: Schematic of how the transport properties of magnetic wires on an insulator could be measured with a probe microscope. Using a mask, a metallic contact that partially covers the wires could be deposited on the sample. Then, the probe tip could be used as the other contact to measure, for instance, changes in the resistance as a function of applied magnetic field. In this case, the absolute value of the resistance would be determined primarily by the resistance of the tip/wire and overlayer/wire contacts. Four-point probe techniques are usually used to circumvent this problem, but would be technically challenging to apply in this case.

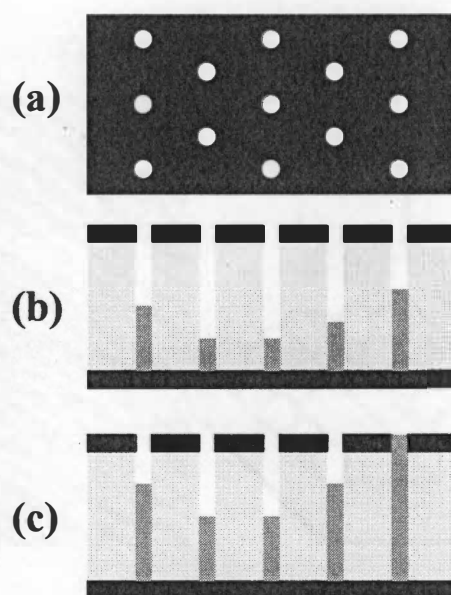


Figure 5.2: A common scheme for observing conductivity in single nanowires. (a) Top view of a nanoporous substrate with a metallic overlayer. (b) Side view of the system while metallic nanowires are electroplated in the pores. (c) When the first wire reaches the top metallic layer, the area of the anode is increased drastically. This results in a sharp increase in the electroplating current. The growth process is immediately stopped at this stage.

electroplating is then immediately stopped, allowing two-probe measurements of the transport properties of a single nanowire.

Further progress was made by Vila *et al.*, who synthesized magnetic nanowires in a template of nanoporous polycarbonate, dissolved the template in dichloromethane (CH_2Cl_2), leaving free-standing nanowires in solution [11]. Spilling a drop of this solution onto a Si substrate left isolated wires, which could be found with scanning electron microscopy. Then, electron beam lithography was used to fabricate the six connection probes shown in Fig. 5.3. This made it possible to perform accurate measurements of transport along different segments of the same wire and provided enough probes to compensate for the contact resistance between the probes and the nanowire. A similar approach is being planned for studying magneto-transport in free-standing FePt nanowires [12].

These approaches have already made it possible to observe the interesting relationship between the creation and annihilation of domain walls and the transport properties of 1-D magnetic nanostructures. Fig. 5.4 shows a two-step jump in the resistance that occurs as a 35 nm diameter, 20,000 nm long Co nanowire is taken from a saturated, single-domain magnetic state through a configuration with one and then two domain walls, and then finally saturated in the opposite direction [7]. Each of the observed jumps in the resistance is believed to be due to the creation of magnetic domain walls as shown in the MFM image to the right.

In Chapter 1, we discussed how the interfaces between two magnetized layers and a non-magnetic spacer show field-dependent conductivity, or "spin-valve" effects. A discussion of the details of the numerous theories [13-16] of how *domain*

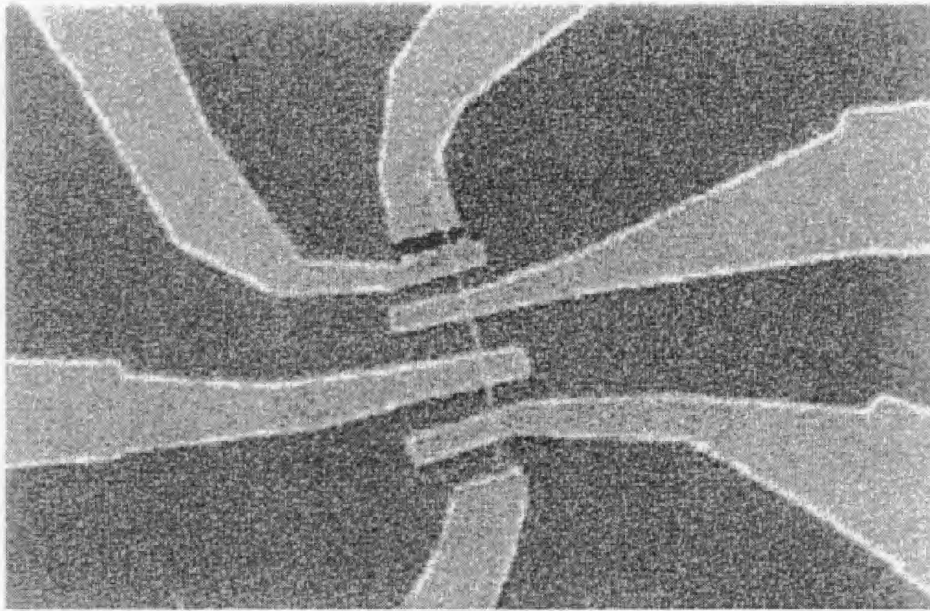


Figure 5.3: Scanning electron micrograph of a single 35 nm diameter cobalt nanowire and lithographically synthesized contact probes [from ref. 6].

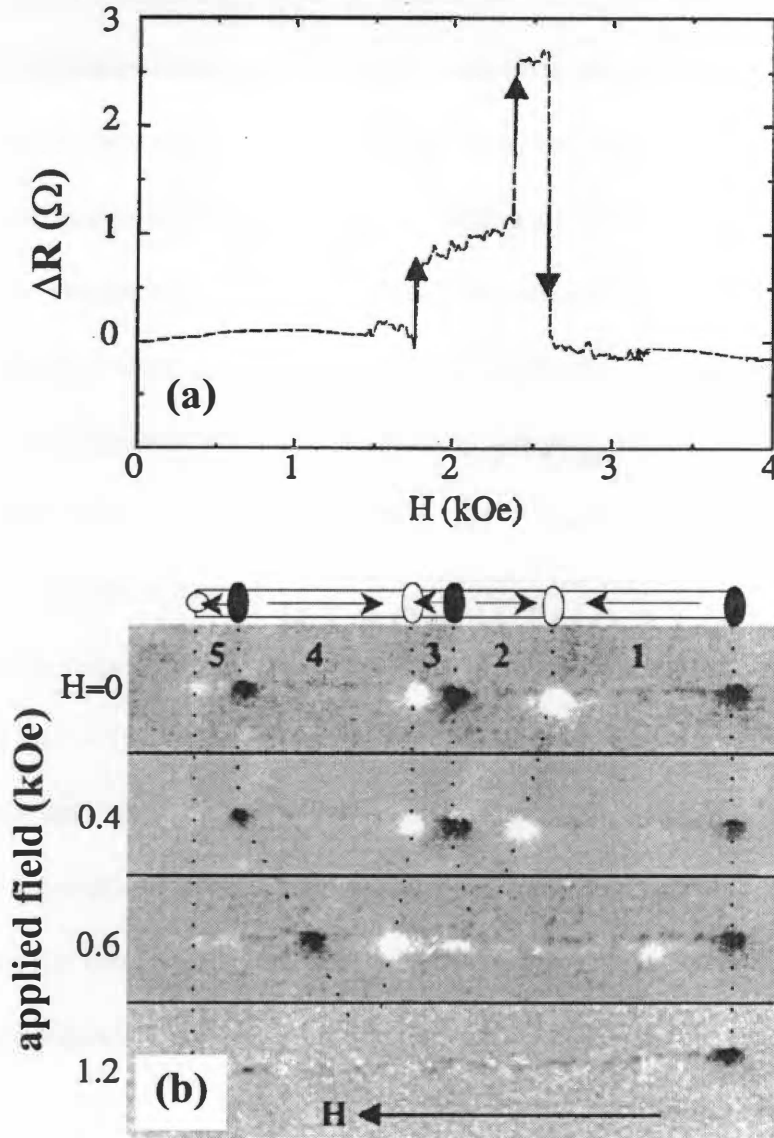


Figure 5.4: Two-step jump in the resistance of a 35 nm diameter Co wire and MFM images of its domain structure [from ref. 2]. (a) Plot of the change in resistance of a single Co nanowire as its magnetization is reversed from one state of saturation to the other. First, two domains of the opposite magnetization form. Then the domain walls are annihilated, leading to a single domain state, and the drop in resistance that occurs at about 2.5 kOe. (b) MFM image of a process in which four domain walls are annihilated as the value of the field applied to the wire is increased. figure shows the similarity between a ferromagnetic domain wall and a tri-layer film

walls in a *single* magnetic material can lead to these same effects is beyond the scope of this chapter, but one can get a feel for how this could happen from Fig. 5.5. The figure shows the similarity between a ferromagnetic domain wall and a tri-layer film sandwich of the sort used in GMR spin-valves. This similarity shows why the absence or presence of domain walls in a magnetic nanostructure can cause field dependent conductivity. In passing through a magnetic domain wall, the spins of the transport electrons cannot respond quickly enough to the changing orientation of the local magnetization. Because the spin-quantization axis is changing ("spin-up" is generally taken to be along the direction of the local magnetization) in the region of the domain wall, the transport electrons, which were formerly spin-up, begin to have a more difficult time passing through the material. Whether or not this explanation is accurate, the important thing is that it is experimentally the case that that these "spintronic" effects are not limited to heterogeneous GMR multilayers shown in Fig. 1.3 in Chapter 1. Giant magnetoresistance effects have been found in several different single element nanowires, including the Co wires that we discussed above, and has also been observed in 1000 Å thick Co films [13].

In this chapter, we will report on the initial steps that we have made in this field in nanostructuring a magnetic material on an insulator [17-18]. We find that by depositing Fe on a freshly cleaved NaCl(100) surface at an elevated temperature (530 K), we can produce isolated iron particles that are amazingly uniform in size. These particles tend to form chains in areas of the substrate where there are atomic step edges. Future experiments like the one shown in Fig. 5.1 could confirm whether or not these chains form continuous wires. Near the end of this chapter, we include our

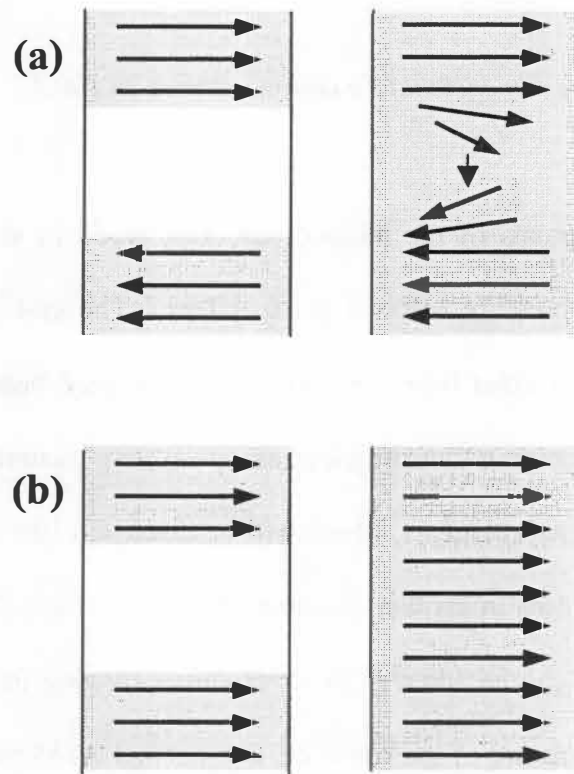


Figure 5.5: Schematic of the similarity between a spin-valve sandwich structure and a ferromagnetic domain wall [from ref. 8]. (a) An anti-aligned spin-valve and a ferromagnet with one domain wall. (b) The spin-valve in the aligned state and the ferromagnet in a single domain state. This similarity indicates why strong field-dependent conductivity is not limited to multi-element structures.

(very preliminary) results on the magnetic behavior of the Fe/NaCl system.

5.2 Morphology and magnetism of Fe films, wires, and dots on NaCl(100)

5.2.1 Synthesis of low-dimensional Fe nanostructures on NaCl

The measurements of the morphology were made in an ultra-high vacuum system with a base pressure below 1×10^{-10} Torr. The system is equipped with thermal and laser molecular beam epitaxy and a combined beam-deflection atomic force microscope / scanning tunneling microscope system manufactured by Omicron, Inc. The magnetic measurements, which will be discussed later, were performed on samples that were grown in another chamber. In this *in-situ* AFM/STM system, the sample temperatures can be adjusted to cover values ranging from 13 K to 1500 K. Given the insulating nature of the substrate, non-contact AFM was used in this work to study the surface morphology since we would have been unable to establish tunneling current necessary for imaging with STM.

Immediately after the NaCl single-crystal substrates were cleaved, they were mounted on a sample holder in a small auxiliary vacuum chamber that was used as a loading dock for the main ultra-high vacuum chamber. Over the next 60 minutes, this load-lock chamber was evacuated to a pressure in the 10^{-7} Torr range. The samples were subsequently transferred to the UHV chamber, in which they were annealed to 530 K for one hour in order to desorb water molecules and other surface contamination prior to the experiments. Figure 5.6 is a typical non-contact AFM

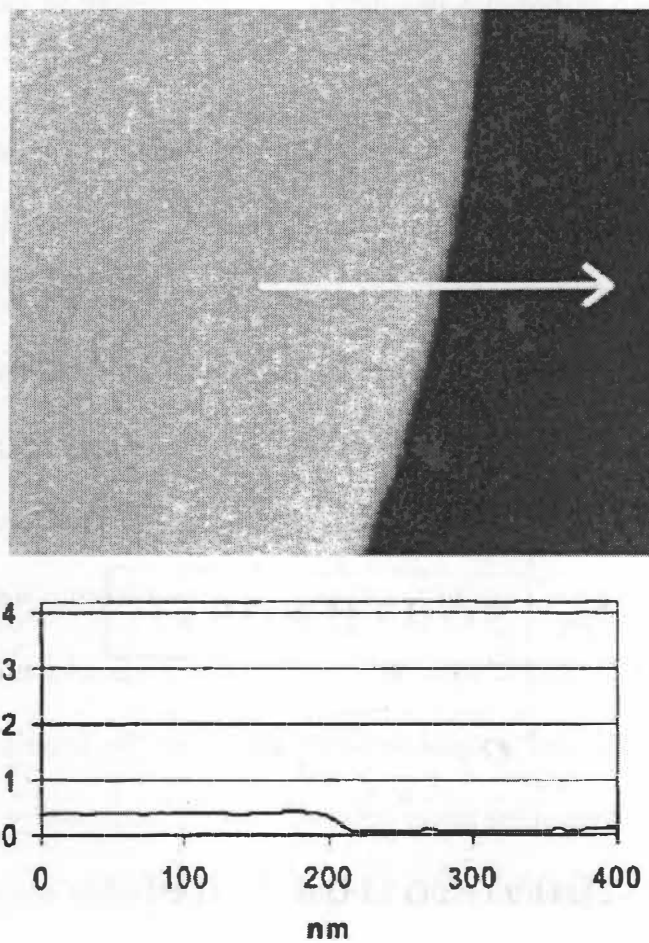


Figure 5.6: Typical non-contact AFM image of the cleaved NaCl (100) surface. The linescan shows atomically smooth terraces separated by the height of a single atomic layer.

image of the cleaved NaCl(100) surface. Iron was deposited on this surface via evaporation of high purity Fe wires, which was accomplished with electron beam bombardment as

described and shown in Fig. 3.3 in Chapter 3. The pressure in the chamber never exceeded 2×10^{-10} Torr during evaporation.

Different nanostructures can be produced on the NaCl surface, depending on the value of the substrate temperature during growth. Figure 5.7 shows the AFM morphology of 0.5 ML of Fe when it is deposited on NaCl at 550 K. Evidently, this high growth temperature allows Fe atoms to move about on the surface until they find other Fe atoms and form clusters. On the flat atomic terraces of the surface, these clusters seem to be randomly distributed and are uniform in size, as shown in the image and line scan at the right of the figure. Wherever atomic step edges exist on the surface, these dots form chains, as shown in the image at the upper left of the figure. The coexistence of isolated dots and chains on the same sample surface is shown in the AFM image at the lower left.

When Fe is deposited on this surface at a much lower temperature, smooth films can be produced instead of these dot and wire structures. A comparison of the morphologies of 1.7 ML Fe prepared at 550 K and 30 K on the NaCl(100) surface can be seen in Fig. 5.8. Apparently, using a low growth temperature restricts the motion of the Fe atoms to such an extent that a very high nucleation density is established. This results in the formation of a film whose corrugation for this coverage is around 0.3 nm, which is on the order of the height of a single atomic step (0.284 nm) on the NaCl surface. Histogram analysis has shown that the layer fillings for the 1.7 ML

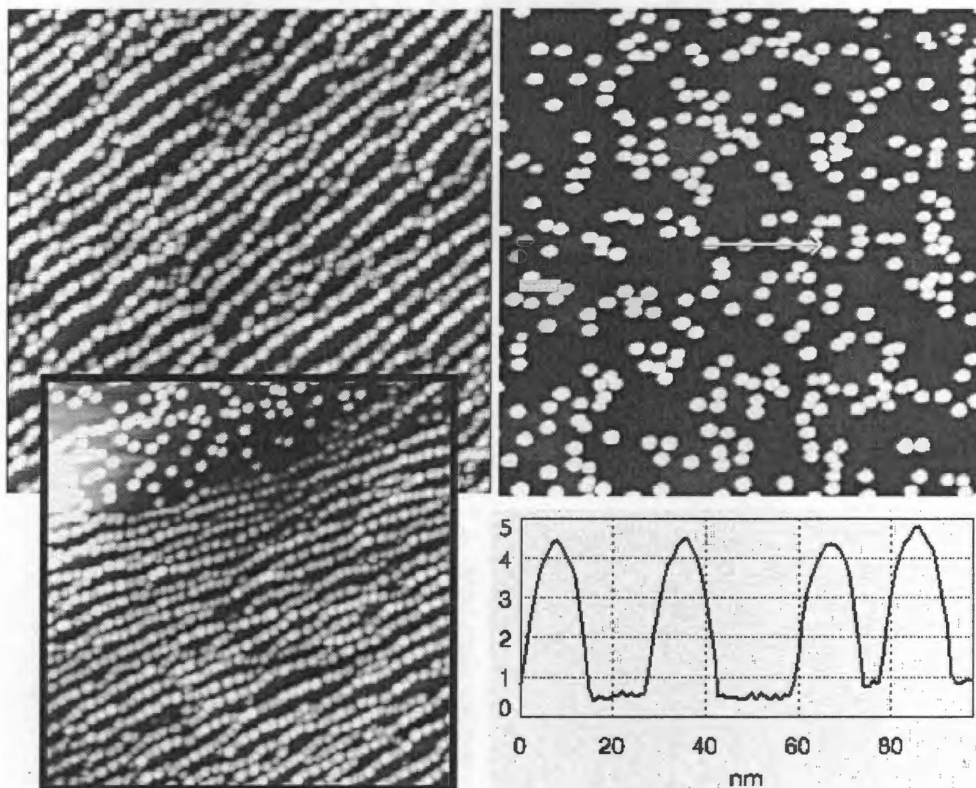


Figure 5.7: AFM morphology of 0.5 ML Fe deposited on NaCl at 550 K. Each of the three images shown is $400 \times 400 \text{ nm}^2$ and was recorded at room temperature. (upper left) Fe tends to form uniform clusters that collect along the atomic step edges of the substrate. (lower left) This STM image shows the coexistence of chains of Fe clusters that form along the atomic steps of the substrate and isolated clusters that form on atomically flat areas. (upper right) STM image and corresponding height profile (lower right) that shows that the dots are nearly identical and approximately 4 nm high. The widths of the dots are probably exaggerated due to tip broadening effects, as discussed in Fig. 1.6 in Chapter 1.

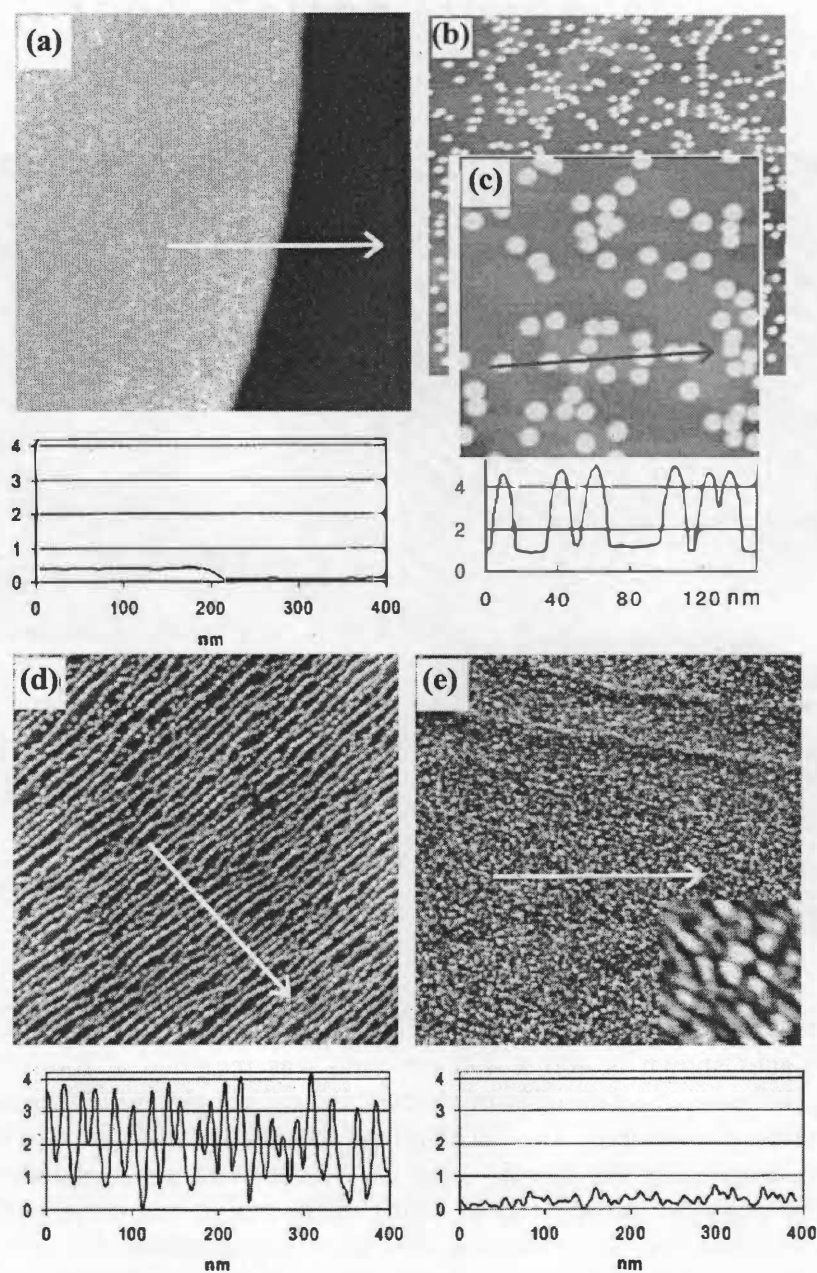


Figure 5.8: Dots, wires, and a film prepared from 1.7 ML Fe on NaCl. The height profiles below each image make it possible to compare the morphologies of (a) the substrate, (b) and (c) a dot assembly found on a substrate terrace, (d) a wire array found on an area of the substrate with parallel atomic steps, and (e) an ultrathin film. The height profiles make it easy to see the drastic difference in morphology that results when the growth temperature is changed from 530 K (as in images b, c, and d) to 30 K (as in image e). Images in (a), (d), and (e) are all $750 \times 750 \text{ nm}^2$.

Fe/NaCl(100) film are 97%, 60%, and 10%, for the first, second, and third atomic layers above the substrate, respectively. For comparison, we note that wires that are also made from 1.7 ML of material exhibit a corrugation that is approximately ten times larger.

5.2.2 Magnetism in low-dimensional Fe nanostructures on NaCl

Sodium chloride is quite different from the Cu substrates that we used in Chapters 3 and 4 in that it is transparent to visible light. As shown in Fig. 5.9, a chip from a silicon wafer was mounted on the back surface of the NaCl crystal to be used as a mirror. This made it possible to conduct magnetic measurements in the reflection (Kerr) geometry. We elected to do this instead of working in the transmission (Faraday) geometry because the location of window ports in our vacuum system did not make it feasible to perform the experiments in transmission.

Before we describe the SMOKE measurements, we briefly note a complication that arose during our initial attempts to run these experiments. We typically used electron bombardment to heat samples in this vacuum system. To accomplish this, we normally biased the sample mount to +700 V and passed a current through the heater filament (see Fig. 5.9) that was behind the sample. This resulted in an emission current of about 50 mA of thermionically emitted electrons between the filament and sample. This type of heating was found to be detrimental to the NaCl surfaces, leaving them with a frosted appearance and/or a slight purple hue. In the early 1970s, in research meant to determine whether or not it was safe to store

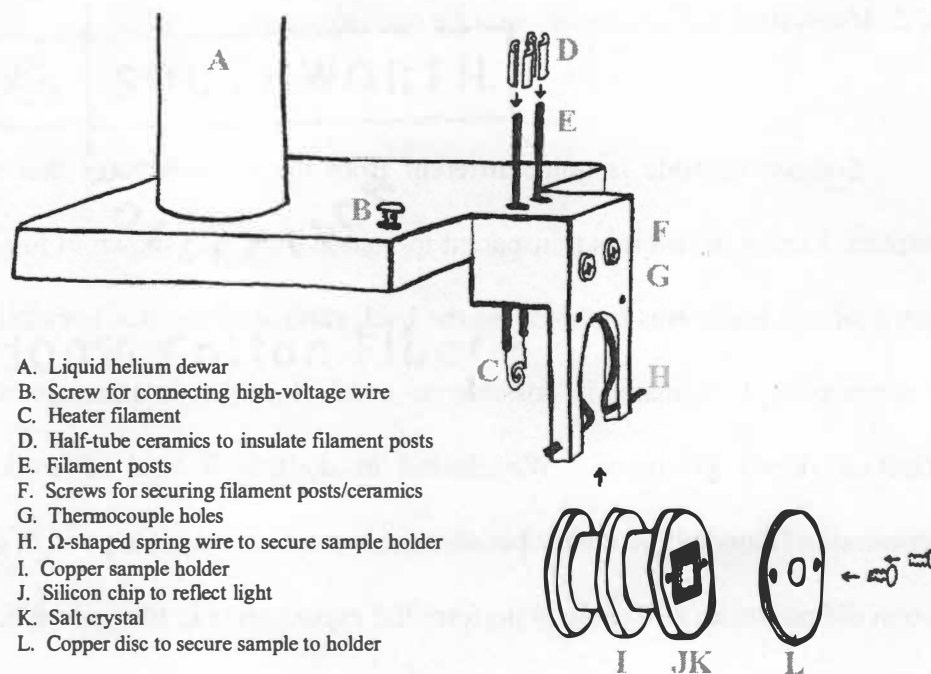


Figure 5.9: Sample mount used in SMOKE experiments on Fe/NaCl samples. The hole in the copper disc (L) allowed the laser to hit the salt sample (K) and reflect off of the silicon mirror (J).

radioactive materials in salt mines, researchers at Oak Ridge National Laboratory found that low energy electrons (0-300 eV) could desorb chlorine ions from the NaCl surface [19-20]. This left vacancies (so-called "f-centers") and, in more extreme cases, needles of pure sodium metal on the surface [20]. The effects that we were observing on our crystal were probably related to this phenomenon. Electrons from the heater filament and/or our pressure gauge filament were attracted toward the surface when the sample was biased. To remedy this, we turned off the pressure gauge and heated the sample via radiation from the heater filament. When this procedure was followed, the surface remained optically clear.

Our preliminary surface magneto-optic Kerr effect (SMOKE) measurements indicate that magnetic ordering in Fe dots, wires, and films on NaCl is much weaker than it is in similar nanostructures on the Cu(111) surface. The tiny paramagnetic response shown in Fig. 5.10 is indicative of the behavior observed in all samples prepared in the thickness (< 5.0 ML) and temperature (> 530 K) regime in which dot and wire formation is known to proceed. Fe dots and wires made from 0.8 ML on Cu(111) showed much stronger ferromagnetic response than we observed in dot and wire structures on NaCl at all coverages. Of the manifestations of Fe/NaCl, the ultrathin films showed the greatest tendency toward magnetic ordering. The dependence of the magnetic response of Fe films on their thickness at 95 K is shown in Fig. 5.11. The films do not begin to show non-zero remanence until they become at least five atomic layers thick. For comparison, we note that a rectangular hysteresis loop is easily observed for a 0.8 ML film of Fe on the Cu(111) surface at this temperature.

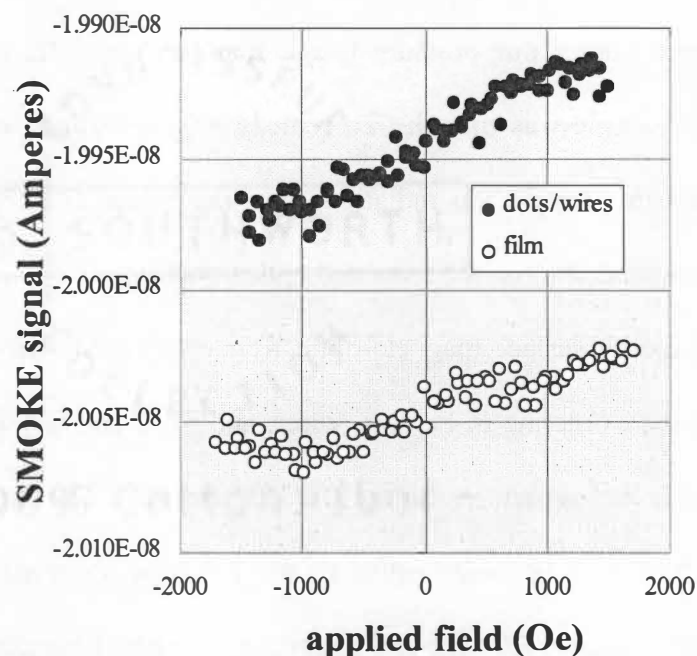


Figure 5.10: Weak paramagnetic response observed from both dots/wires and a film prepared from 4.2 ML Fe on NaCl. The curve generated by the filled circles corresponds to a sample in which the iron was deposited with the sample held at 530 K, which was the growth temperature at which the formation of dots and dot chains was found to occur. The other curve corresponds to a sample prepared below 30 K, which is in the regime in which single-layer-rough films form. The upper curve was recorded at 32 K and the bottom curve was measured at 35 K.

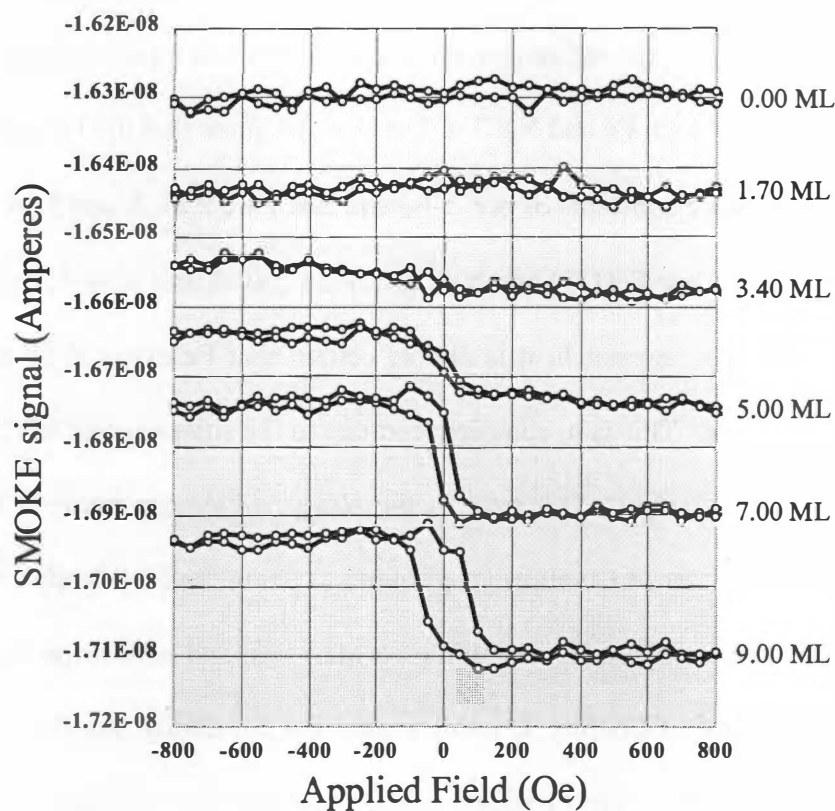


Figure 5.11: SMOKE hysteresis loops of various amounts of Fe on NaCl at 95 K. No magnetic response can be resolved when the thickness is 1.7 ML or lower, and no remanent magnetization is observed for films below 5 ML at this temperature. The curves have been shifted vertically so that they can be viewed on the same plot.

There are at least two reasons why magnetic ordering is decreased to such an extent in Fe nanostructures on NaCl relative to that of those on Cu(111). The first reason may be that the Fe atoms in the films and in the clusters that form the dots and wires on the NaCl surface are arranged on a different lattice grid than they are on Cu(111). The lattice structure of a material determines its magneto-crystalline anisotropy which, in turn, influences its magnetic behavior (see Chapter 2). The lattice mismatch between Fe and NaCl is 37.6% if we guess that the Fe assumes a bcc structure. (The lattice constants of bcc α -Fe and NaCl are 2.87 Å and 5.64 Å, and the nearest neighbors of bcc Fe(110) and NaCl(100) are 2.49 Å and 3.94 Å, respectively.) Because of this large mismatch, it is almost certain that Fe exists in its natural bcc phase on this surface. This is in complete contrast to the situation on Cu(111). As we discussed at the beginning of Chapter 3, the close relationship between the fcc Fe lattice constant and that of Cu allows the copper to strain the Fe in such a way that it is stabilized in the fcc phase in very thin (< 6 ML) film and nanostripe structures on Cu(111). At the end of Chapter 4, we discussed the possibility that the influence of the copper substrate may even be strong enough to induce fcc structure in the dots, as well.

The second reason for the reduced tendency toward magnetic ordering in iron on NaCl may be the fact that the substrate is an insulator. This would discourage any magnetic stability that might result from dot-dot interactions mediated by the polarization of substrate electrons. These possible “RKKY-type” interactions are similar to the interlayer coupling effects that were described in Fig. 1.4 in the first chapter. In systems that show this type of interaction, the moment of a magnetic

object sets up a disturbance in the net polarization of the electrons of the surrounding, non-magnetic medium. This disturbance decays with distance from the magnetic object, but is known to strongly influence the relative directions of the moments other, nearby magnetic entities. While these effects may be present on a copper substrate, their presence can be ruled out on an insulator.

Given the relationships that are being discovered between resistivity and the presence of domain walls in magnetic nanostructures (see section 5.1), the transport properties of Fe/NaCl(100) nanowires could be particularly interesting. These wires are unique in that they are formed from chains of discrete clusters. Given the physical structure of the dot chains, it is likely that the domain size in the dot chains could be as small as the individual clusters, which are much smaller than the domains observed in magnetic nanowires discussed in section 5.1. This means that a particular length of these chains could contain more domain walls in the absence of an applied field (at remanence) than the other wires, and would therefore shown an even larger magnetoresistance. The wires could also be of interest because the domain walls will be more likely to form at the particular locations in the wires where the identical clusters meet. This would discretize the sizes of the domains, which would be determined by how many consecutive dots were magnetized in the same direction.

Probing the magnetic properties of these wires with a technique that can resolve domains would probably be more fruitful than the preliminary SMOKE studies that we have performed. At their current level of performance, however, techniques like MFM and SEMPA do not have the resolution to see individual domains in these closely packed wires. Obtaining useful results with these techniques

would become much more feasible if the wires were prepared on a NaCl template whose atomic steps were further apart. In the results shown in this chapter, the salt crystals were cleaved by hand with a sharp metal blade, which meant that we had relatively little control over the distribution of flat terraces and atomic steps. As shown in the AFM images in Fig. 5.7, this method of preparation tended to produce both step-free areas and areas in which the atomic steps were tightly bunched together. Recently, attempts have been made to produce surfaces that could produce wires that would be more suitable for magnetic imaging. One approach for producing regular, parallel step edges that are several times further apart than those in Fig. 5.7 is to precisely orient the crystal with Laue x-ray diffraction and polish it to a particular miscut from the (100) plane with a mixture of ethanol and water [21]. The latest AFM images of surfaces prepared in this way are encouraging.

5.3 Final remarks

In the last decade, both materials scientists and condensed-matter physicists (the distinction between the two is becoming less clear) have taken two approaches to develop new, functional materials. One approach, as discussed in this dissertation, has been nanostructuring simple materials to awaken complexity in and functionality in them. Another approach has been to *begin* with complex materials. (At present, particularly "hot" classes of complex materials include biological systems, polymers and composites, and certain transition metal oxide (TMO) compounds. The latter class of materials has attracted interest because it has been found that small changes

in an external parameter, like the applied field or the temperature, can induce drastic and unpredicted changes in their electronic, structural, and magnetic behavior that absolutely cannot be described by textbook physics.) It is clear that these two approaches will *merge* in the coming decades; complex materials will be nanostructured and this will awaken new levels of complexity and functionality in them.

What new properties would we find if we could join two nanowires of dissimilar materials end to end? What effects could we observe with just the right sequence of magnetic metal and semiconductor segments? Can half-metallic complex materials (those which show metallic behavior for spin-up electrons, but insulating behavior for spin-down electrons) be fabricated as nanowires? The degree to which their transport properties could be switched by an applied magnetic field would be tremendous. What interesting behavior could we see in crossed magnetic wires? We are only able to ask ourselves these questions because of the incredible progress that condensed-matter physicists and chemists have made in nanostructuring materials.

Nanostructuring has introduced us to a new frontier of tunable, artificially structured materials. In this exciting new area we control how the atoms or layers of atoms are arranged in materials. The goal in this area is to develop this power over materials and to understand how it enables us to awaken useful properties in them. This goal has been the subject of this thesis. In Chapter 3, we found ways in which the magnetic properties of ultrathin films, wires, and quantum dots could be systematically varied in order to teach us about their behavior. In Chapter 4, we saw

how creative synthesis can let us see how the behavior of a single material changes as it is spatially confined in one, two, and three directions. In the upcoming decades, it will be novel approaches like these, along with continued leaps in our ability to synthesize and characterize on the nanoscale, that will build our intuition and eventually our mastery of these materials.

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Appendix

A.1 Ultrahigh vacuum (UHV)

Objects like ultrathin films, nanowires, and quantum dots have to be prepared in an ultra-clean environment. Since these structures consist, at most, of only a few layers of atoms, it is unacceptable to prepare them in the atmosphere that we live in since unknown quantities of unknown contaminants easily become incorporated in them. A rule of thumb is that for every 10^{-6} Torr of ambient pressure that a material is exposed to, the number of atoms that strike the surface is such that if each atom stuck upon contact, one atomic layer of contamination would form every second. (For this reason, a useful unit of gas exposure, the "Langmuir" is defined as $1 \text{ L} = 10^{-6} \text{ sec} \cdot \text{Torr}$.) This means that in order to have roughly one hour to study a sample before an atomic layer of contamination forms, the residual gas pressure should generally be below 10^{-9} Torr. Most of the experiments in this dissertation were performed in vacuum chambers in which the background pressure was below 9×10^{-11} Torr. The chambers in which most of the SMOKE and probe microscopy studies were performed are shown in Fig. A.1(a) and A.1(b), respectively.

High-vacuum environments are also necessitated by the fact that many of the techniques used in studying surfaces involve beams of electrons. Two of these techniques, low-energy electron diffraction and Auger electron spectroscopy, were discussed in Chapter 3. Electrons are used because their penetration depth in solids is less than several atomic layers if their kinetic energies are moderate (1-1000 eV). This makes them inherently surface sensitive. If the ambient pressure was too high,

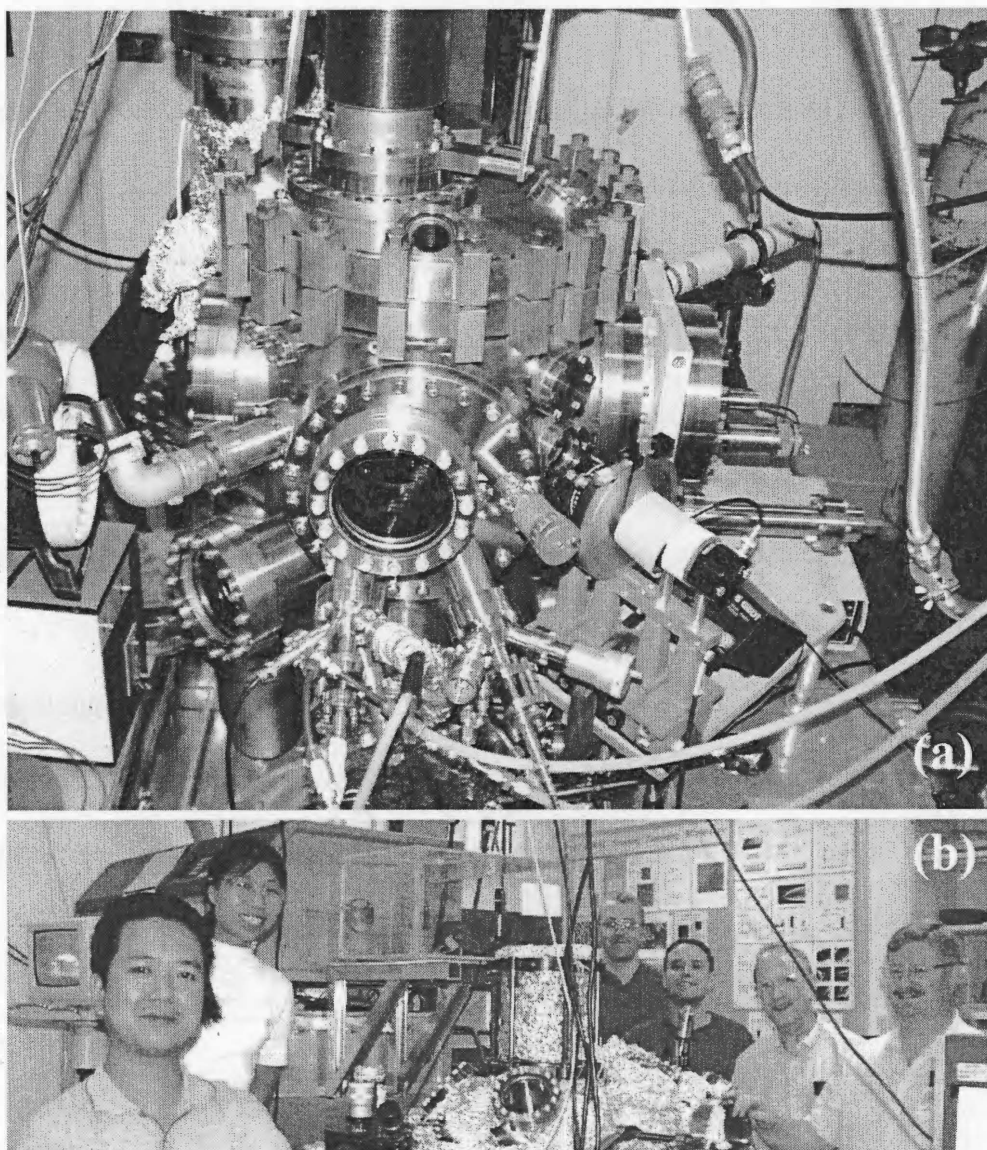


Figure A.1: The ultra-high vacuum systems that were mainly used in our studies. (a) The UHV chamber in which our SMOKE studies were conducted. (b) The variable-temperature STM/AFM system, surrounded (from left to right) by Jian Shen, Zheng Gai, Gareth Farnan, the author, John Wendelken, and Art Baddorf.

electron beams would not survive their journey through the space between the instruments and the sample.

When a typical stainless steel chamber is evacuated, the pressure tends to plateau in the 10^{-7} Torr range, which is still too high for an experiment to be conducted in a reasonable amount of time. The pressure plateaus in this range because of the H_2O , CO, CO_2 , hydrogen, and oxygen molecules that slowly leave the chamber walls. In order to improve the pressure, the chamber is wrapped with fiberglass-insulated heating wires, completely covered with aluminum foil to insure even heating, and "baked" for a day or two at a temperature of approximately $150^{\circ}C$. During the "bakeout" the contaminants desorb from the hot chamber walls and are pumped away. On the day that the chamber is allowed to cool, current is passed through each of the filaments that belong to the various instruments in the system. This degassing process insures that the amount of contamination that will be introduced later as the filaments are used in actual experiments is minimal.

The pumps used to provide the UHV environment for the work in this thesis included turbomolecular pumps, titanium sublimators, ion pumps, and cryopumps. Turbomolecular pumps are essentially VERY high speed fans. They rotate at $> 20,000$ rpm. When gas molecules enter the turbopump, the rotating blades impart momentum to them that drives them away from the vacuum chamber. As a new graduate student, it was surprising to find out that a *titanium wire* could be a *pump*. To use a titanium sublimation pump (also known as a TSP, or as a "getter" to the older folks), one runs enough current through a titanium wire to resistively heat it until it begins to sublime. The ejected titanium atoms coat the layers of

contaminants on the walls of the vacuum system and tend to bind reactive gasses like hydrogen and oxygen. Ion pumps consist of filaments, strong permanent magnets, and titanium plates. Electrons that leave the hot filaments via thermionic emission are confined to tight spiral orbits by the fields of the permanent magnets. The spiraling electrons can ionize background gas atoms, which are attracted to 700 V biased titanium plates. These ions either become buried in the titanium and/or blast titanium atoms off of the surface of the plates, creating an effect similar to that of a TSP. A cryopump is simply a container that is located within the vacuum chamber but can be filled with liquid helium or nitrogen from outside of the chamber. The principle behind cryopumping is exactly the opposite of the principle behind baking a vacuum chamber. When the container is filled with cryogenic liquid, its walls become cool enough to trap most of the gas molecules that happen to bump into it. Later, when the experiments are finished and the container is warmed, most of the gas molecules that had been "frozen" to its surface are allowed to desorb.

A.2 Using the surface magnet-optical Kerr effect (SMOKE)

A.2.1 Observing Kerr rotation and ellipticity

Using the SMOKE is amazingly simple. As shown in Fig. A.2, a laser beam is directed through a polarizer and at the surface of a sample that is placed between the poles of a magnet. As was discussed in Chapter 2, the axis along which the incident beam was polarized undergoes a slight rotation upon reflection if the sample

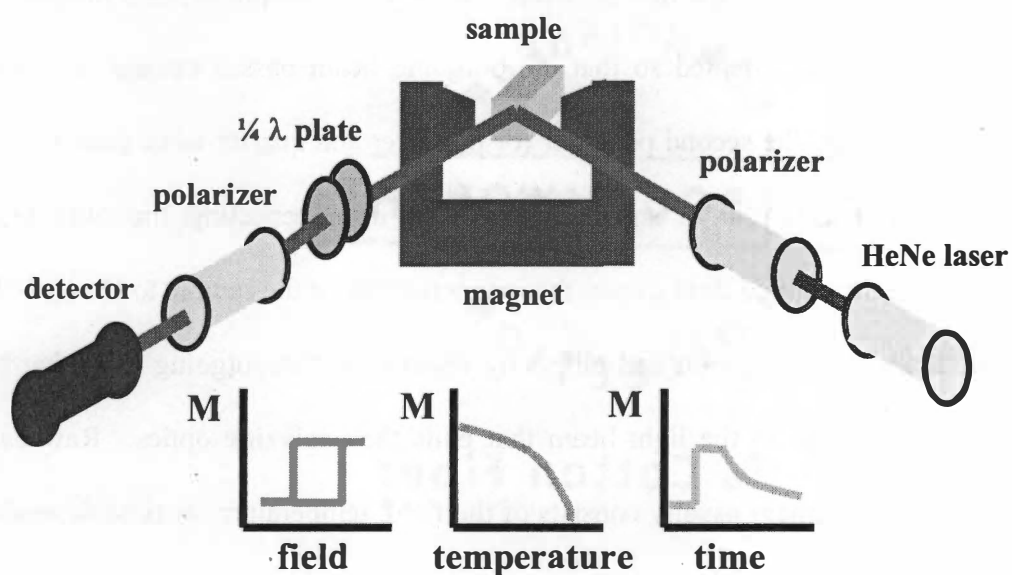


Figure A.2: Schematic of our SMOKE apparatus. The magnet and sample are contained within an ultrahigh vacuum chamber that is not pictured here. As shown above, this technique makes it possible to record the magnetic response of a material as a function of applied magnetic field, temperature, and time.

is magnetized. In addition, the incident beam picks up a slight ellipticity. By using a second polarizer or a polarizer and a quarter waveplate, this rotation or this ellipticity can, respectively, be observed as a change in the intensity of the outgoing beam.

First, in order to maximize the number of photons incident on the sample surface, it is wise to first make sure that the plane of polarization of the HeNe laser coincides with that of the first polarizer. Second, the sample is positioned in the path of the beam and oriented so that the outgoing beam passes through the analyzing optics. Finally, the second polarizer (or polarizer and quarter wave plate) is oriented such that it is within a small angle ($1-4^\circ$) from canceling the outgoing light. Sweeping the applied field causes the magnetization of the sample to change. This, in turn, leads to polarization and ellipticity changes in the outgoing light that become intensity changes in the light beam that exits the analyzing optics. Raw data in a SMOKE experiment usually consists of the field, temperature, or time dependence of the light intensity.

For reference, and to clarify what is happening, the relationship between the polarization and ellipticity changes due to the Kerr effect and the intensity observed in a SMOKE experiment will be developed here. The approach shown here closely follows that given in ref. [17] from Chapter 1, a review article written by the creator of the modern form of the technique.

Suppose we align the analyzing polarizer in Fig. A.2 such that it is a small angle (δ) from eliminating light which is polarized along the y -direction. (See Fig.A.3, as well.) In this configuration, the electric field of the outgoing light will be

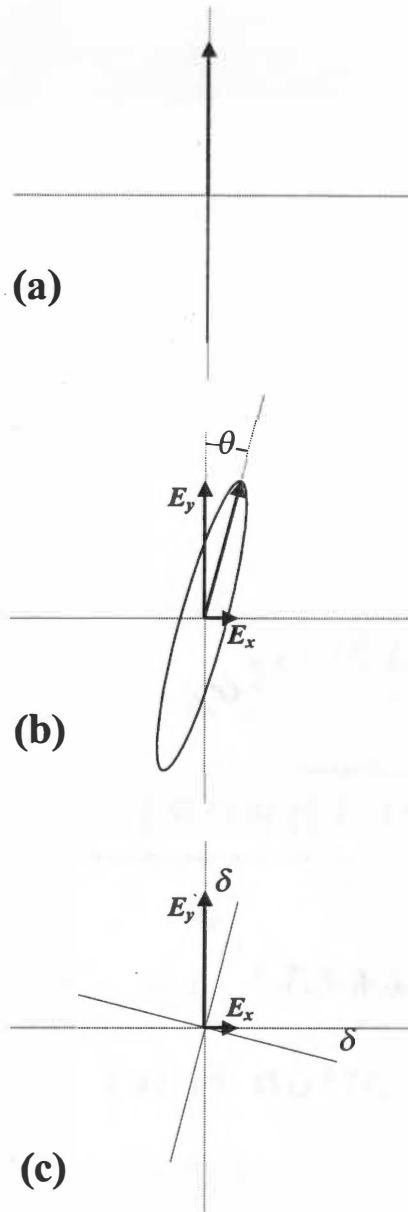


Figure A.3: Kerr rotation and ellipticity. (a) For the example discussed in the text, we assume that the incoming light is polarized with its electric vector along the y -direction. (b) The plane of polarization of the outgoing light is rotated by θ_r , the real part of the complex Kerr angle θ . The outgoing light also has a slight ellipticity due to the phase difference between the x - and y -components of its electric vector. This phase difference is given by θ_e , the imaginary part of θ . (c) To observe the polarization rotation (or ellipticity) as an intensity, we insert a polarizer (or polarizer and quarter waveplate) in the path of the outgoing beam such that the polarizer is at an angle δ from extinction of the outgoing light. The rotation of the plane of polarization and the ellipticity are greatly exaggerated in this figure.

$$\vec{E} = E_y \sin \delta + E_x \cos \delta$$

and becomes

$$\vec{E} = E_y \delta + E_x$$

if the angle δ is very small.

If the sample carries no net magnetization, there will be no E_x component of the field. However, if the sample is magnetic, then the reflected light will pick up a small component E_x that is given by

$$E_x = E_y \tan \theta \approx E_y \theta$$

in which θ is a small, complex angle. If we separate this angle into its real and imaginary parts, we have

$$\theta = \theta_r + i\theta_e$$

The angle θ_r is called the "Kerr rotation" and is due to changes that occur in the real part of the index of refraction of the sample as it is magnetized. The angle θ_e is called the "Kerr ellipticity" and results from changes in how the material absorbs light (changes in the imaginary part of the index of refraction) as it is magnetized.

This gives us

$$E_x = E_y (\theta_r + i\theta_e)$$

and

$$E = E_y(\delta + \theta_r + i\theta_e)$$

If we square the field to find the intensity (I) that will be read by the detector, and neglect all terms that are of order θ_r^2 and θ_e^2 , we find

$$I = |E|^2 = |E_y|^2(\delta^2 + 2\delta\theta_r)$$

If we define I_o to be equal to $|E_y|^2\delta^2$, which is the intensity when there is no Kerr effect, we find that

$$I = I_o\left(1 + \frac{2\theta_r}{\delta}\right)$$

Solving for the Kerr rotation gives

$$\theta_r = \frac{\delta}{2} \frac{(I - I_o)}{I_o}$$

The value of the Kerr rotation at maximum field is

$$\theta_r^{\max} = \frac{\delta}{2} \frac{(I_+ - I_-)}{(I_+ + I_-)}$$

Where I_+ and I_- are the intensities observed when the applied field is at its largest positive and negative value, respectively.

It is possible to measure the Kerr ellipticity by inserting a quarter waveplate, as shown in Fig. A.2. The quarter waveplate retards one component relative to the other by $\pi/2$ radians. Therefore, the outgoing light wave picks up a phase change given by

$$e^{-i\left(\frac{\pi}{2}\right)} = \cos\left(\frac{\pi}{2}\right) - i \sin\left(\frac{\pi}{2}\right) = -i$$

The Kerr angle becomes

$$\theta = (\theta_r + i\theta_e)(-i) = -i\theta_r + \theta_e$$

so, we obtain

$$E = E_y(\delta + \theta_e - i\theta_r)$$

Again, we square the field to find the intensity. This gives us

$$I = |E|^2 = |E_y|^2(\delta^2 + 2\delta\theta_e^2)$$

if we neglect terms which contain θ_r^2 and θ_e^2 as before. If we again define I_0 to be equal to $|E_y|^2\delta^2$, which is the intensity when there is no Kerr effect, we find that

$$I = I_o \left(1 + \frac{2\theta_e}{\delta} \right)$$

Proceeding exactly as before, we can solve for the Kerr ellipticity at saturation.

$$\theta_e^{\max} = \frac{\delta (I_+ - I_-)}{2 (I_+ + I_-)}$$

The equations for θ_r and θ_e establish the relationship between the observed intensities and the Kerr rotation and ellipticity.

A.2.2 The relationship between Kerr rotation/ellipticity and magnetization

In Chapter 2, we used a simple form of the conductivity tensor to show that the off-diagonal elements of this tensor lead to magneto-optical effects. More generally, one can use the dielectric tensor to derive formulae that describe what is observed in a SMOKE experiment. The dielectric tensor is related to the conductivity tensor via the relation

$$\varepsilon(\omega) = \varepsilon_0(\omega) + \frac{4\pi i \sigma(\omega)}{\omega}$$

Using this approach is more general because it contains both σ , which describes the response of electrons in partially filled bands (conduction electrons) and ε_0 , which

describes the response of electrons in filled energy bands (like the core electrons).

For a ferromagnet, an appropriate form of the dielectric tensor is

$$\varepsilon = \varepsilon \begin{pmatrix} 1 & im_z Q & -im_y Q \\ -im_z Q & 1 & im_x Q \\ im_y Q & -im_x Q & 1 \end{pmatrix}$$

Here, m_x , m_y , and m_z are the components of the magnetization and Q is called the "Voigt constant" and depends on the properties of the material. The important thing to note is that the off-diagonal elements, which will ultimately lead to magneto-optical effects, are related linearly to the magnetization. To proceed, one assumes that an electromagnetic wave is incident on the sample and solves Maxwell's equations under the usual constraints (normal D , tangential E , normal B , and tangential H are all continuous across any boundaries). While the process is conceptually simple, couplings of the field components that are introduced by the off-diagonal tensor elements render this problem algebraically complex. As the derivations are long and have been shown in great detail elsewhere (see Chapter 1 ref. [17] and references therein), we will present the results that have been relevant to this dissertation.

(1) *In ultrathin films, SMOKE intensities are directly proportional to the component of the total moment that lies in the optical plane.* Calculations reveal that the Kerr rotation (θ_r) and ellipticity (θ_e) are directly proportional to the off-diagonal elements in the dielectric tensor. These tensor elements, in turn, are linear in the magnetization. In the previous section, we showed that observed intensities in a

SMOKE study are linear in θ_r and θ_e . From this, the result that the observed intensities are linear in the sample magnetization can be inferred. This behavior is verified by numerous experiments. Examples can be found in the data shown in Chapter 4 in Fig. 4.17. This proportionality breaks down when the film thickness becomes comparable to the penetration depth of the light.

There are three distinct geometries that can be used in SMOKE experiments. Each of the three is pictured in Fig. A.4. In polar SMOKE, the applied field is perpendicular to the plane of the sample surface. In the longitudinal geometry, the magnetization lies in the plane of the sample and in the plane of the incident and reflected light beam. Those are the two geometries that have been used in the experiments presented in this dissertation. In the transverse geometry, the magnetization also lies in the plane of the sample, but is perpendicular to the optical plane. No Kerr rotation or ellipticity is observed in this configuration, due to the orthogonality of $\mathbf{M}$ and the optical plane.

(2) *The Kerr effect is roughly an order of magnitude greater in the polar geometry than it is in the longitudinal geometry.* For a single ultrathin film (in which the film thickness d is much smaller than the wavelength of the light) of refractive index n on a substrate of refractive index n_{sub} , the complex Kerr angles for the two geometries are found to be

$$\theta^{polar} \propto \left(\frac{n^2}{1 - n_{sub}^2} \right) d$$

$$\theta^{longitudinal} \propto \left(\frac{n_{sub}}{1 - n_{sub}^2} \right) d$$

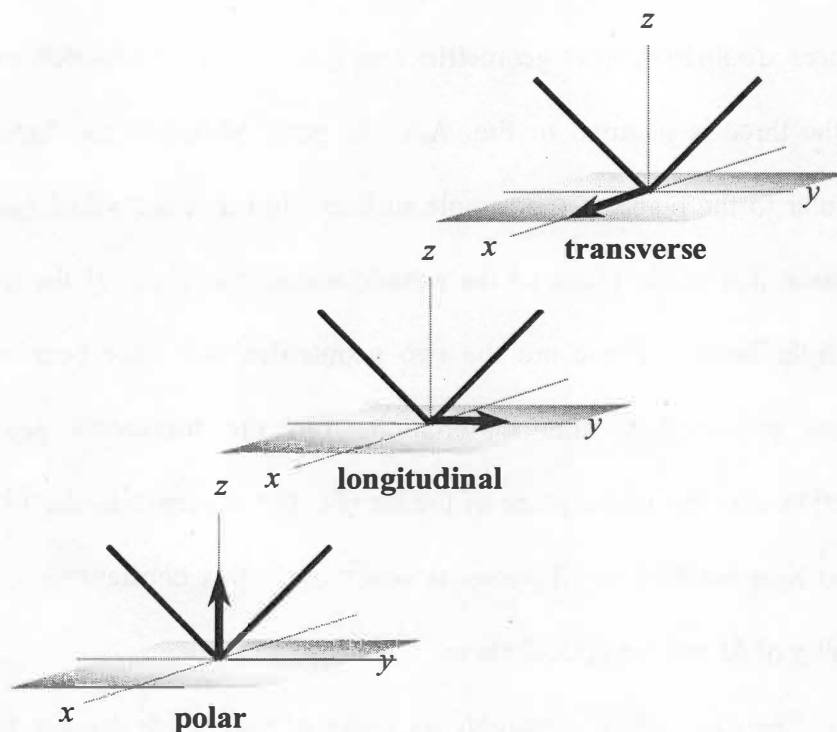


Figure A.4: Three configurations for SMOKE studies. Assuming that the sample surface lies in the xy plane and that the reflection of the laser occurs in the yz plane, one is working in the polar geometry when $\mathbf{M}$ lies along the z -direction, the longitudinal geometry when $\mathbf{M}$ lies along the y -direction, and the transverse geometry when $\mathbf{M}$ lies along the x -direction. No polarization rotation/ellipticity is observed in the transverse geometry since $\mathbf{M}$ does not have a component in the optical (yz) plane.

The extra factor of n in the polar Kerr angle contributes to the increased signal in that geometry.

Intensities observed in the two geometries can be normalized to each other if the moments of the sample can be driven to saturation in both cases. By definition, if the magnetization is saturated in a particular direction, every moment in the sample is forced to point along that direction. The value of the saturation magnetization should, therefore, not depend on the direction. The longitudinal Kerr intensity can be multiplied by a constant to force its value at saturation to equal that observed in the polar geometry. This compensates for the optical factors that reduce its value relative to the polar Kerr intensity. This normalization was used in our attempts to compare the moments of the film, nanostripe, and dot array configurations of Fe on Cu(111) in section 4.3.2 (see Fig. 4.17 in that section).

A.2.3 Magnet

Magnets made from superconducting materials are becoming increasingly popular. Since electromagnets, however, are simpler to construct, cheaper, and provide fields that are large enough for most studies, they continue to be more commonly used in SMOKE systems. These magnets typically consist of a coiled wire that surrounds a c-shaped "yoke" of material. The coil provides magnetic flux lines when current is passed through it and the yoke focuses these lines and concentrates them in the region of space between the arms of the "c", making the applied field much higher than it would be if coils of wire were used alone.

The magnet used in our studies was an electromagnet made of a c-shaped vanadium permendur yoke wrapped with kapton-coated wire. Vanadium permendur was chosen because it is an incredibly "soft" magnetic material. It is not soft in a mechanical sense, but in a magnetic sense in that it exhibits a very narrow, tall hysteresis loop. This means that it is easy to switch its moments and that it shows very little magnetization when the coil current that magnetizes it is removed. This type of material was ideal for our purposes since we wanted a one-to-one correspondence between a particular applied current and the resulting magnetic field. This material was also useful in that its magnetic moment doesn't saturate until it is subjected to an enormous field (23,000 Oe). This meant that as we applied more current, more and more moments in the material were able to keep contributing to the flux density between the pole pieces.

In practice, our maximum operating field was limited to 2000 Oe by the fact that we needed to preserve the ultrahigh vacuum environment for our experiments. When current was passed through the magnet, energy was, of course, dissipated at a rate given by $P = I^2R$, in which R is the resistance of the coil wire. This resistive heating was enough to cause various gasses to desorb from the kapton-coated wire. This problem has been solved in newer magnets used in our research group in which the coils are enclosed in a vacuum-tight metal shroud through which cooling water can be passed.

The gap between the pole pieces of our magnet was 0.68" or 17.3 mm. The relationship between the coil current and the resulting applied field at the center of the pole pieces was established with a Hall effect probe. It was determined that for

relatively applied fields (< 200 Oe), a field equal to 6% of this field remained when the current was reduced to zero. This 6% factor was improved upon when higher fields were applied. These remanence effects were accounted for in our analysis of the data.

Vita

John Philip Pierce was born in Lansing, Michigan on March 18, 1975. He attended public schools in Michigan in the cities of Lansing, Kalamazoo, and Okemos, and graduated from Okemos High School in May of 1993. For the next four years, he studied physics and chemistry at Albion College, a liberal arts college in Albion, MI. He held summer research appointments at the University of Michigan in 1995 and at the University of Tennessee, Knoxville in 1996 before graduating *summa cum laude* and earning a Bachelor of Arts degree in Physics at Albion in May of 1997. Upon the award of a joint fellowship from the University of Tennessee and Oak Ridge National Laboratory in the summer of 1997, he began graduate studies in the areas of surface physics and magnetism in nano-scale structures. He earned his Ph.D. in Physics in May of 2003 and, as of this writing, is looking forward to an exciting future.

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