As described in our original proposal, we have spent the final year of our research program investigating the physical properties of nanometer-scale magnets. This has involved several projects and associated experimental techniques.
May 6, 1996

Dr. Harold Weinstock
Air Force Office of Scientific Research
Physics and Electronics
110 Duncan Avenue, Suite B115
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20332-0001

Dear Harold,

The following pages contain the final technical progress report for our Grant #F49620-93-1-0117, "Physical Properties of Nanometer-Scale Magnets", as required by the Air Force Office of Scientific Research.

Please contact me if you require additional information.

Sincerely,

David D. Awschalom
Professor of Physics
AFOSR Technical Progress Report
Grant #F49620-93-1-0117
Final Technical Report

"Physical Properties of Nanometer-Scale Magnets"

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1. Research Review during the final grant period

As described in our original proposal, we have spent the final year of our research program investigating the physical properties of nanometer-scale magnets. This has involved several projects and associated experimental techniques, each of which is described in turn below.

Imaging and Magnetometry of Mesoscopic Magnets

Arrays of nanometer-scale iron particles are grown by local organometallic deposition with a scanning tunneling microscope. The average magnetic properties are studied at low temperatures (5 – 100 K) with a two-dimensional hole gas Hall magnetometer. Rotation of the net array magnetization occurs by both reversible and irreversible modes, the latter revealed by Barkhausen jumps. Direct spatially-resolved measurements at room temperature with a magnetic force microscope show that the discrete jumps are due to the sudden switching of individual single-domain particles. Particles that appear structurally similar are found to be magnetically distinct.

The present work employs the additive technique of local organometallic deposition with a scanning tunneling microscope (STM) to produce nanometer-scale iron particles with control of the shape and orientation. The average magnetic properties of an array of particles is compared with the properties of individual particles by complementary low temperature Hall magnetometer and room temperature magnetic force microscope (MFM) measurements, the latter producing some of the highest resolution magnetic images of submicron structures to date. Although the particles formed with the STM are seen to be structurally similar through atomic-scale topographic studies, they vary magnetically in terms of coercive fields, suggesting that anisotropy on a length scale smaller than the spatial resolution of our probes (~25 nm) is playing an important role.

The Hall magnetometer provides a measure of the average magnetic properties of nanometer-scale particles, but requires care in interpretation since particles are not weighted equally. Imaging of individual particles with an MFM explores the current limits of scanning probe microscopy. Although the STM forms particles that are ostensibly similar in structure, magnetically there is found to be a distribution of coercive fields through direct imaging. Magnetic properties may ultimately serve as a more sensitive characterization of nanometer-scale particles, as demonstrated also by the identification of a magnetic film formed concomitant with the growth of the STM particles. However, the effect of the MFM tip on small particles can be significant. One of the outstanding challenges is the development of magnetic probes which are less invasive.
Femtosecond Near-field Spin Microscopy in Digital Magnetic Heterostructures

A detailed understanding of spin scattering in mesoscopic electronic systems remains, for the most part, an open issue in condensed matter physics. To directly investigate the dynamic behavior of electronic spin, one needs to develop both a host material in which the fundamental spin interactions are well understood, and techniques for probing spin scattering on the relevant time and length scales. Extensive research in recent years has identified II-VI magnetic semiconductor quantum structures as flexible systems in which to study electronic spin interactions in a well-characterized environment. In such systems, the strong exchange coupling between electronic states and paramagnetically aligned magnetic ions results in large effective Landé g-factors at low temperatures ($g_{\text{eff}} \sim 400$ at $T=4$ K). Quantum well (QW) confinement enhances by several orders of magnitude the coupling of excitonic states to visible light, enabling a wide array of optical techniques to be used. The Zeeman splittings in recently grown structures can be made much larger than inhomogeneous linewidths, providing model field-tunable two-level systems ideal for magneto-optical studies of spin-dependent phenomena.

Conventional time-resolved optical spectroscopies have successfully probed dynamical spin-dependent phenomena in this class of structures, yielding important information about exciton spin scattering and magnetic relaxation. However, to examine directly the role of interfaces, alloy fluctuations, disorder, local magnetic environments, impurities and defects on excitonic spin transport -- factors which involve spatial degrees of freedom -- one requires a technique capable of resolving the relevant physical lengthscales, from exciton diffusion lengths ($\sim 1 \mu$m) to magnetic correlation lengths ($>50$ nm in antiferromagnetically ordered MnSe), to the exciton Bohr radius ($\sim 4$ nm for ZnSe/ZnCdSe). Conventional optical techniques, being diffraction limited, cannot provide sufficient resolution on the lengthscales of interest. Near-field scanning optical microscopy (NSOM) circumvents the diffraction limit and, combined with femtosecond-resolved spectroscopies, provides a unique capability of interrogating spatio-temporal excitonic spin dynamics in magnetic semiconductors.

Static and time-resolved luminescence studies of excitonic spin behavior in magnetic semiconductor QWs have been performed using a low-temperature polarization-resolved NSOM. A series of patterned defects, introduced by Ga$^+$ focused-ion-beam implantation, reduces both the QW luminescence intensity and the local $g$-factor, creating a magnetic-field-driven, spin-dependent energy landscape for diffusing excitons. Carrier spin distributions are inferred from the near-field images of the DC luminescence intensity and polarization. Exciton diffusion is found to have a minimal effect on the local magnetic interactions which contribute to Zeeman split states. The incorporation of time resolution, using a luminescence intensity correlation technique, provides additional evidence for spin-dependent exciton diffusion. Time-resolved absorption, another powerful tool, provides direct information about the spatiotemporal evolution of photoexcited excitons. Fundamental limitations on the measurement of polarized luminescence from semiconductors in the near field are demonstrated and discussed.

Submicron Ferromagnets in Mn-implanted III-V Semiconductors

Microscopic ferromagnets can be fabricated on semiconductor substrates in a number of ways, including electron-beam lithographic patterning, scanning tunneling microscope deposition, and electrochemical etching and electrodeposition. In order to enhance the effective interaction between electronic carriers and local ferromagnetic
fields, it is desirable to locate ferromagnetic clusters within a semiconductor. This is a challenge since the solubility of magnetic ions in semiconductors is generally low. Because Mn ions replace Ga in the GaAs lattice and act as acceptors, it is possible to incorporate localized ferromagnetic structures inside the GaAs semiconductor while preserving its electronic and optical properties. This may be achieved by ion implantation and subsequent heat treatment. Although the solubility of Mn ions in GaAs is very low under equilibrium conditions, a relatively high concentration (~10^{21} cm^{-3}) can be obtained by implanting the ions into the semiconductor. During rapid thermal annealing at T > 600°C, the uniformly implanted Mn ions diffuse and combine with Ga to form submicron GaMn microcrystallites (150 - 400 nm) which are ferromagnetic at room temperature. A structure containing an ensemble of particles has a magnetization that can be reversed at the coercive field \( H_c \sim 6 \) kOe, and becomes paramagnetic above the Curie temperature \( T_c \sim 400 \) K. These particles are larger than the typical magnetic particles (1 - 10 nm) in granular GMR materials and in fact, large enough that the magnetic moments may not be uniform throughout the particle, i.e., the particle consists of magnetic domains. In this instance, the GaAs host plays an important role in determining the magnetic properties such as the domain orientation.

The GaMn ferromagnets are formed near the GaAs surface and may be directly probed by atomic (AFM) and magnetic force microscopy (MFM) at room temperature. In MFM images, the contrast is caused by spatial variations in the magnetic interaction between the magnetized probe and the stray magnetic fields of the sample. While the ferromagnetic particles (~400 nm) produce strong magnetic force contrast, there exist particles (~50%) which show only weak contrast. The latter particles are likely ferromagnets with very low coercive fields and moment densities or possibly even superparamagnets at room temperature.

One can infer the magnetic state of the GaMn precipitates from these MFM images. To a good approximation, the MFM probe behaves like a localized magnetic dipole, and the imaging of spherical single-domain particles can be modeled by a dipole-dipole interaction. We have calculated single particle images based on this approximation for several different configurations. A more detailed model which integrates dipole moments over the surface of the tip produces similar node structures. These simulations show that one can obtain a variety of patterns from a single-domain particle, depending on the relative orientation between the tip and particle moments. However, with a perpendicularly magnetized tip, such as is used to produce the data in, the simulations of single-domain particles do not show the complicated four-component contrast observed. Thus, these two precipitates must be multi-domain magnetic particles, while the others are single-domain particles. Such simulations demonstrate the importance of understanding the interplay between instrumental sensor and sample cluster magnetic fields for meaningful particle imaging in mesoscopic dimensions.

In an unmagnetized sample, particles within this length scale can be single-domain or multi-domain. In a field, multi-domain GaMn particles are converted to single-domain particles; in particular, the single-domain moments are observed to preferentially align along the three equivalent crystalline axes (<100>, <010>, <001>) of the GaAs host after the field is removed. The behavior of ferromagnetic particles can also be studied by continuously applying an in-plane field. For fields stronger than the tip coercive field (~400 Oe), the tip is forced to align with the in-plane field, thus allowing simple image interpretation. As the in-plane field is increased, the moments tend to align with the field direction, displaying two types of motion: discontinuous reversal and gradual rotation of the magnetization, depending on the relative orientation between the magnetic easy axis and the applied field.

These processes can be investigated directly by imaging single particles in real time while ramping the in-plane applied field. A large variation (about a factor of three) in the switching field is also found among particles with approximately the same easy
axis orientation. As these particles are likely to have the same crystalline structure with similar strain, this variation may be due to shape anisotropy. Further investigations should reveal the magnetic anisotropy and micromagnetic behavior of these single-domain magnets as well as their role in modifying electronic transport.

**Mechanical Detection of Magnetism: Microfabricated Cantilevers**

The fabrication of very delicate mechanical cantilevers combined with sensitive displacement detection schemes has resulted in a number of remarkably powerful experimental techniques, including scanning force microscopies, mechanically detected magnetic resonance, and a new class of torque magnetometers. In general, the force sensitivity of these techniques can be improved by lowering the spring constant \( k \) of the cantilever (thereby increasing the displacement per unit force) and increasing the resonant frequency \( n_0 \) (decreasing the necessary averaging time). Since most semiconductors and metals have mass densities and elastic moduli within an order of magnitude of each other, the design parameters that afford the greatest opportunities for improvements are the physical dimensions of the cantilever. Specifically, for a rectangular cantilever, one can achieve small \( k \) and large \( n_0 \) by simultaneously decreasing all the dimensions.

Typically, micron-scale cantilevers are fabricated from silicon, silicon oxide, or silicon nitride. Fabricating cantilevers from the GaAs/AlxGa(1-x)As materials presents challenges in designing new processes for the III-V chemistry. More importantly, it offers the advantages of integration with optical devices, magnetic systems, and strain sensing elements that utilize the piezoelectric properties of the GaAs to detect the cantilever displacement. Cantilevers fabricated from the III-V semiconductors have usually contained Al-rich layers (included as part of a laser structure), which simplify the fabrication of free mechanical structures by allowing the selective etching of the GaAs substrate out from under the Al-rich layers. During this period we have successfully designed a process for making cantilevers from a single epilayer of GaAs grown by molecular beam epitaxy (MBE) on an AlAs etch stop layer on a [100] GaAs single crystal substrate. We have fabricated cantilevers 100 nm thick, comparable to the thinnest cantilevers fabricated from silicon and much thinner than cantilevers previously fabricated from GaAs/AlGaAs. This process allows easy access to both sides of the cantilever by etching a window through the entire thickness of the GaAs substrate, unlike previous GaAs/AlGaAs cantilever processes. We have characterized the resonant frequency, quality factor \( Q \) and spring constant of a 100 nm thick GaAs cantilever fabricated in this fashion.

To construct very thin cantilevers made of a single material (as opposed to GaAs/AlGaAs layers), we use MBE to grow a 100 nm thick GaAs epilayer on a 300 nm thick AlAs epilayer on a [100] GaAs substrate. The GaAs epilayer will ultimately form the cantilever, and so its thickness determines that of the cantilever; the AlAs serves as an etch stop and a sacrificial layer. The lateral shape of the cantilever is defined by optical lithography in photosist spun on the epilayers. In the present case, the pattern is of the form of a window with a cantilever extending into the window. This pattern provides protection to the cantilever against damage in later fabrication steps as well as in actual use. This pattern is then etched into the epilayers by a Cl₂ reactive ion etch.

The cantilevers were mounted on a piezoelectric crystal and driven over a range of frequencies in order to measure \( n_0, k, \) and \( Q \). Here we take \( Q = (Dn / n_0) \), where \( Dn \) is the FWHM of the cantilever response. Their displacement was measured using laser interferometry. The response of a 135 mm long, 30 mm wide and 100 nm thick cantilever as a function of the driving frequency at room temperature and pressure shows a resonant frequency of 4.5 kHz and a \( Q \) of \( \sim 2 \). Note that this value is expected to increase by several orders of magnitude in vacuum, as the lever is heavily damped under atmospheric...
conditions. In addition, we have measured the absolute magnitude of the Fourier transform of the (undriven) noise in the interferometer. The technique of measuring the thermal noise of the cantilever has many advantages over the driving approach, in particular the fact that the spectral weight of the thermal noise tends to select the "soft" (small k) modes and reject the large k modes, which include the modes of the mounting itself, whereas the response of a mode to the piezo driving force is insensitive to the mode's k. The thermal noise gives values of n0 and Q that are consistent with the piezodriven measurement. Because of the cantilevers' large aspect ratio and low mass, air damping limits the Q. The thermal noise of the same cantilever at a pressure of 250 mTorr shows that n0 has increased to 5.1 kHz and Q to ~ 9. From this value of the resonance frequency, we find k ~ 10^-4 N/m. This spring constant is smaller than for any other cantilever of which we are aware. Given a DC displacement sensitivity of 1 nm, this results in a DC force sensitivity of ~ 10^-13 N.

We intend on exploiting the sensitivities of these microfabricated detectors to explore the classical and low temperature quantum spin dynamics in mesoscopic quantum magnetic spin systems grown through chemical techniques. In particular, new single crystals of iron-based molecular magnets have been grown in a collaboration between the physics and chemistry departments at UC-Santa Barbara. Crystals of molecules containing 8,10, or 12 iron atoms have been grown by crystallization from solution and characterized by x-ray diffraction and angle-resolved SQUID magnetometry. The iron atoms within these molecules are arranged in different configurations and are magnetically coupled to each other by superexchange through organic ligands. Depending on the geometries of the molecule, the coupling between spins can give rise to a variety of different ground states. For \( T > 1.7K \), there are no inter-molecular interactions in the crystalline state, and the crystal assembly is an ensemble of identical finite spin systems with calculable, discrete spectra. We will explore the dynamics of the molecular magnetization in pulsed magnetic fields, measure the field-driven spin splitting, and determine the potential for field-tuning coherent tunneling phenomena between energy-degenerate eigenstates.

2. Publications during the final grant period

*Peer-reviewed journal articles*


### 3. Invited Talks during this grant period and accepted invitations


4. Contributed Talks during the grant period and forthcoming


