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**14. ABSTRACT**
Mechanically-milled alloys of iron with cobalt ("Hyperco")and aluminum have been fabricated with a puck-and-saucer mill, and have been studied with the bulk magnetization, differential scanning spectrometry, neutron scattering and muon spin rotation techniques. One as-yet-unresolved problem is that of compaction. Two major discoveries concerning iron-aluminum alloys were made during this reporting period, inverse melting, and the presence of incommensurate static spin-density waves. A laboratory for preparation and characterization of magnetically-ordered materials has been assembled and is still under development. It includes two high-precision field-gradient magnetometers, a differential scanning calorimeter, the puck-and-saucer mill, an annealing furnace, and associated electronics and computers. Several papers were published during this reporting period, and two graduate students are doing their thesis research in this laboratory.

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# Mechanically Milled Iron Alloys for High-Temperature Magnetic and Structural Applications

## Virginia State University

**Supported by AFOSR Grant F49620-00-1-0364**

**Report for the period August 1, 2002 - July 31, 2003**


**Carey E. Stronach**
**Project Director**

**Anthony S. Arrott**
**Scientific Director**

The primary aim of the program on mechanically-milled iron alloys at Virginia State University is to make "Hyperco 27", the alloy of iron with 27 percent cobalt, Fe(27Co), and the highest saturation magnetization known, without its usual drawback of high magnetic anisotropy. This would alloy motors, generators and transformers to operate at the saturation induction. It is also important that Hyperco 27 has excellent high-temperature properties. Hyperco 27 would be the ideal material for the "more electric airplane." There are theoretical reasons to believe that "exchange softening" could be used for the purpose of reducing the effect of the anisotropy. Exchange softening should occur when the grain size is small compared to a characteristic length whose square is given by the ratio of the exchange to anisotropy constants, both of which are intrinsic to any particular material. For Hyperco 27 this is about 30 nm. Grain sizes can be made less than 10 nm by mechanical milling. The effective field from the anisotropy should drop below 0.2 Oe at 10 nm and fall off as the $6^{th}$ power of the grain size for smaller grains. With an 8 nm grain size the material should be quite magnetically soft, allowing the full saturation magnetization to be achieved in electrical applications.

The above is in theory. There are problems. The theory assumes that the grains are dislocation-free single crystals and that the grain boundaries do not matter. A practical magnetic material must be free of defects, of which voids are to be assiduously avoided. The major obstacle in trying to achieve a soft magnetic material starting with Fe(Co) alloys is the extreme mechanical hardness found in the as-milled condition. It was not possible to achieve compactions with more than 65 per cent of full density, where 99.999 per cent was desired. But even with the low-density samples there were strong indications that the individual particles were not magnetically soft.

The two main issues to evolve from these studies are the problem of how to obtain good compaction and the question of the nature of the grain boundaries on the magnetic properties.

The compaction problem requires going to high temperatures to get sufficient plastic deformation, while at the same time avoiding increases in grain size that would remove the exchange softening. One route is to use fast local heating at the contacts between the grains. We intend to pursue pressing mechanically-milled Hyperco with pulsed electrical heating at the asperities. There is an organization in Fairfax, VA called

Materials Modification Inc., who have developed the technique called Plasma Pressure Compaction. We have funds for some test runs using their equipment.

That our mechanically-milled Hyperco has such great resistance to compaction implies that there may be applications where this high yield strength could be used. This result was contrary to expectations. In addition to an exchange softening of the magnetic properties below 30 nm, it was expected by many that a mechanical softening would occur below the range where the conventional hardening with decreasing grain reaches its maximum. The evidence for this from other work is not convincing, so this remains a controversial subject.

We turned to Fe(40Al) to study the properties of grain boundaries. This material is paramagnetic at room temperature in the as-made material, which has normal grain sizes. Fe(40Al) has the B2 CsCl structure, which can be described as two interpenetrating simple cubic lattice complexes, one of which is all Fe and the other has all the Al and the remainder of the Fe atoms. If $Fe_9Al_7$ existed as a fully-ordered structure, none of the iron clusters of eight iron atoms surrounding a single iron atom would have connections to any adjacent clusters, see Fig. 1. That would suppress ferromagnetism completely. It is not surprising then that the partially ordered Fe(40Al) structure is not ferromagnetic as the percolation limit for the propagation of a chain of nearest neighbor Fe-Fe interactions is not achieved below 62% Fe. For a random body-centered-cubic alloy the critical concentration for ferromagnetism is not 60% Fe, but 25% Fe. Thus any disordering of the Fe(40Al) structure leads to ferromagnetism. In particular, an Fe(40Al) alloy with an 8 nm grain size would have perhaps 20% of its atoms in grain boundaries where the structure would be fully disordered and ferromagnetic. In particular, an Fe(40Al) alloy with an 8-nm grain size would have perhaps 20% of its atoms in grain

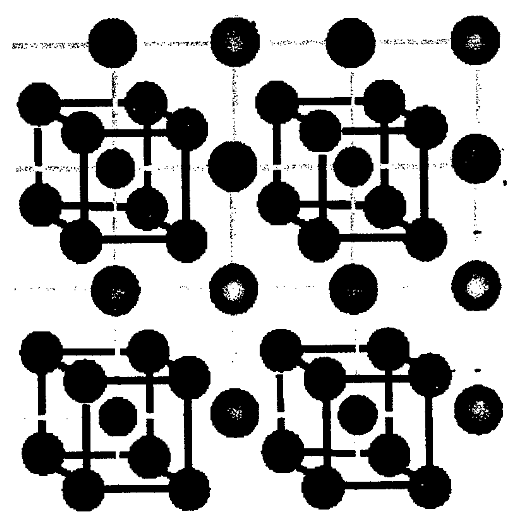

Fig. 1. The structure of hypothetical $Fe_9Al_7$, showing the first three layers in perspective. The Al atoms (large balls) separate the Fe clusters (small balls).

boundaries where the structure would be fully disordered and ferromagnetic. On mechanical milling to 8 nm grain size followed by annealing to recover the ordered structure of the grains, one should achieve paramagnetic grains surrounded by ferromagnetic grain boundaries, forming a magnetic foam. Such a material would be ideal for studying the magnetic nature of the grain boundaries and shed some light on the problem of the grain boundaries in Hyperco 27.

This experiment was carried out. The alloy Fe(40Al) was mechanically milled to produce a fine grain size, approximately 10 nm, and found to be magnetic with a moment of 1.0 $\mu_B$ per atom of Fe compared to 2.2 $\mu_B$ for pure Fe. On annealing to reorder the grains, it was expected that the moment would decrease to that of the 25% of Fe atoms in the grain boundaries. The experiments showed a decrease of less than 25 % rather than a decrease to 25%. It appears that grains themselves do not return fully to the paramagnetic state. This may be a proximity effect of the ferromagnetic grain boundaries polarizing the paramagnetic grains, or it may be that the structure is not as ideal as expected. It appears that to obtain a more foam-like structure, it may be necessary to work at higher Al concentrations. That all this is the case for Fe(40Al) implies that the picture for Fe(27Co) may have similar effects of the grain boundaries on the behavior of the grains.

The work on Fe(40Al) produced two new discoveries. One of these is the occurrence of what has been called inverse melting, or more properly in this case, inverse freezing. The other is the spectacular result that Fe(Al) alloys for concentration of 34, 40, and 43 percent Al show the presence of incommensurate static spin-density waves. This result was not anticipated. For more than 40 years Fe(Al) alloys of these concentrations were deemed to be "spin glasses." Indeed they have all the properties normally associated with the term spin glass, yet by neutron diffraction we were able to show that these also exhibit spin-density-wave antiferromagnetism with the spin-density waves coming in at temperatures far above the spin-glass transition temperature, through which there is complete indifference in the spin-density-wave antiferromagnetism. These results have pervasive ramifications in the theory of condensed matter physics.

The support for the work on iron alloys has made it possible to create a laboratory for the preparation and characterization of magnetic materials. The principle preparation tool is the puck-and-saucer mill used for very high-energy mechanical milling. This

Australian rock crusher has been adapted to our purposes by adding cooling coils, controlled internal atmosphere, and solving the problem of maintaining the pressure seal under impacts of the 6 kg puck at 15 Hz with a kilowatt of power being dissipated in the process. The laboratory has two furnaces for heat treatment, and glass-blowing equipment for sealing samples in controlled atmospheres. X-ray and neutron diffraction studies are carried out at NIST. Magnetization measurements are made using the gradient-field magnetometer developed at Virginia State University and the magnetometers at NIST. The gradient field magnetometer is still under development. The thermodynamic measuring equipment includes a differential scanning calorimeter operating from 300 K to 1000 K and a conventional heat capacity apparatus operating from 1.5 K to 370 K. A small machine shop has been assembled to assist in this work.

There remain problems with the rock crusher. When there were problems of keeping air out of the mill, the nature of the product resulted in uniform coating of the puck and saucer by the milled material. This protected the loose material from contamination by the puck and saucer. When the air was excluded, it changed the nature of the particles sufficiently that the lid of the saucer no longer became coated. This created contamination problems because there was always some of the most recently removed material from the lid that had not yet mixed with the powder. Studies are underway to eliminate this small amount of contamination using Teflon inserts.

The gradient-field magnetometer is a new concept that came from considering how to measure the approach to saturation of the Hyperco alloys. The usual way to measure magnetization has a uniform magnetic field with the sample translated between two detector coils in series opposition. The new method uses a uniform detector coil with the magnetic field produced by two coils in series opposition. This permits rapid and precise measurements over a range of fields without the time consuming process of changing and measuring the field at each step. The spatial variation of the field replaces the variation in time. Position is field. On translation, the sample experiences the full range of fields. The arrangement is shown in Fig. 2.

A pulse tube Cryomech refrigerator to 3 K cools the split-coil superconductor A Daedal linear motor moves the sample with a precision of 10 nm over distances up to 50 cm. The induced voltage in the detector coil is integrated with great precision using a

Keithley 2182 Nanovoltmeter which has a modification suggested by us to the manufacturer that allows for integration over a long enough period to be make it the best possible measuring device for integrating voltages from moving-sample magnetometers. The variable temperature sample environment, still under development, will cover the continuous range of temperatures from 80 K to 1050 K. A permanent magnet with a gradient field from –2.5 T to 2.5 T is being procured. This will make the equipment more economical and convenient for other users and remove the problem with eddy currents generated in the aluminum walls of the superconducting magnet housing. Quantum Technology (Whistler, BC) is undertaking the commercialization of this apparatus.

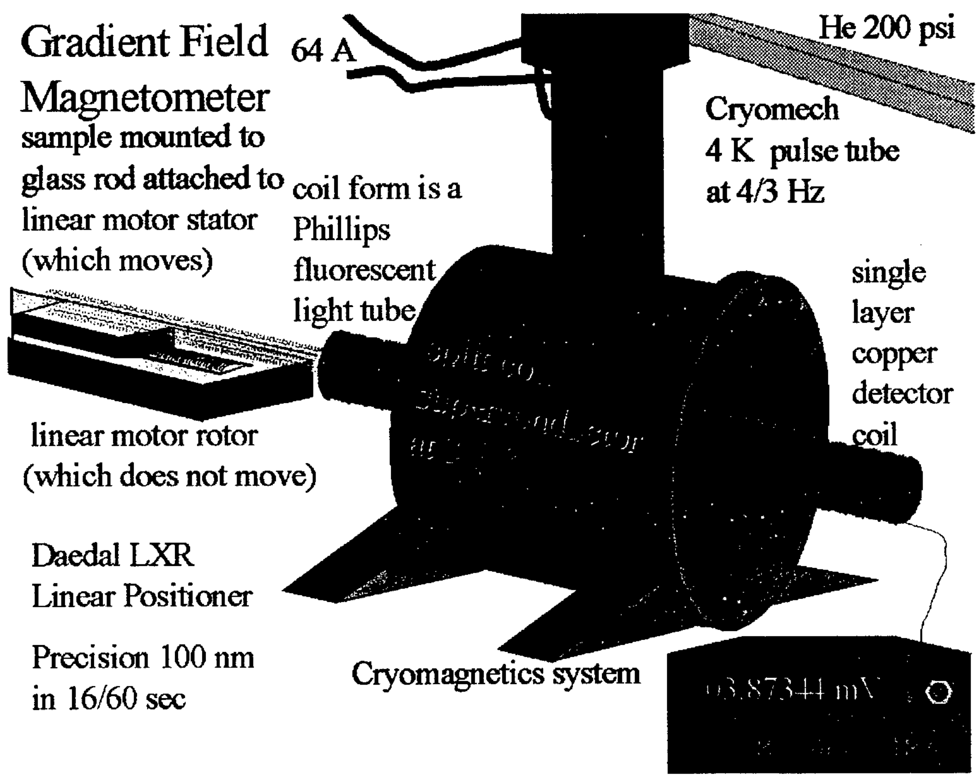


Fig. 2. Layout of the gradient-field magnetometer conceived and developed at Virginia State University.

The utility of the method is illustrated in Fig. 3 for an alnico magnet subjected to a series of minor loops while traversing the major hysteresis loop. This measurement, carried out in a sequence of 700 field points, was performed in 4 minutes.

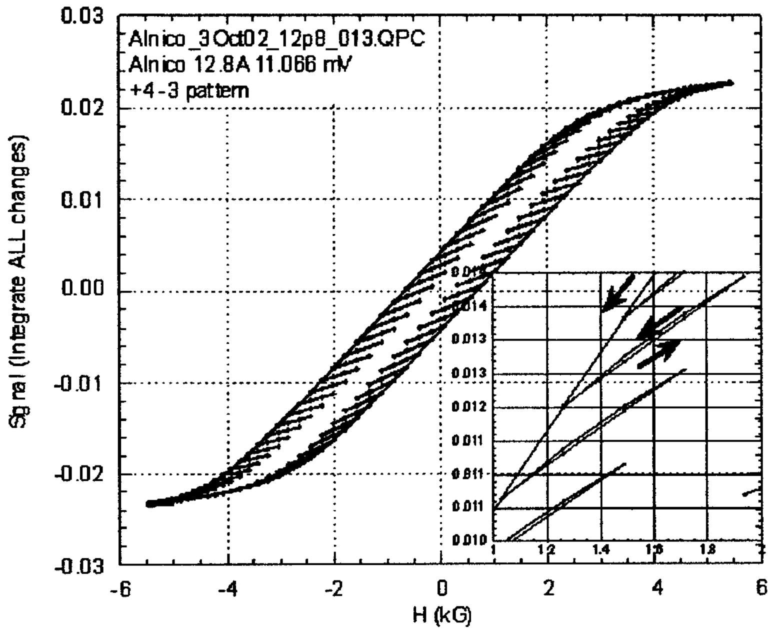

Fig. 3. Major and minor hysteresis loops for Alnico

The concept of a magnetic foam using Fe(Al) alloys came from Prof. Arrott's studies of these alloys in the 1950's, when he investigated how ferromagnetism disappears on increasing the Al content beyond 30 atomic percent. He found the higher aluminum-content alloys to be non-ferromagnetic at ambient temperatures and to have a magnetic freezing temperature into an undetermined antiferromagnetic state at low temperatures; see Fig. 4. In order to prepare his alloys for neutron diffraction measurements, he created small particles by filing. The filings became ferromagnetic at room temperature, but became non-magnetic after heat treatment. This combined with the current studies of mechanical milling lead to the idea that annealing the <10 nm grain size material should produce non-magnetic grains surrounded by grain boundaries that retain ferromagnetism because of the local disorder. The fact that after annealing these powders are more magnetic than expected indicates that there is much to be understood about the properties of these less than foam-like materials.

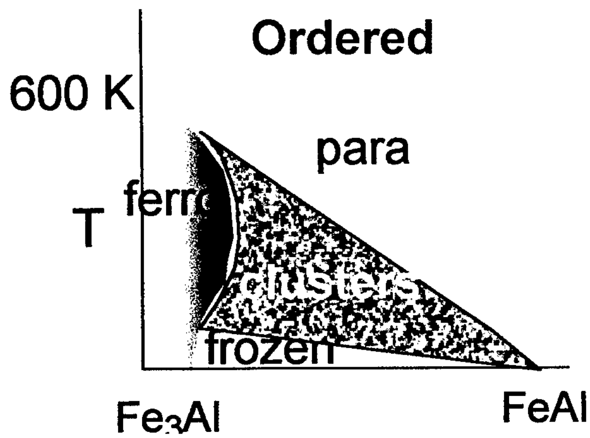


Fig. 4. Magnetic phase diagram for the CsCl structure of Fe(Al) alloys. The reentrant behavior near 30 atomic percent Al has not been satisfactorily accounted for.

As mentioned above, the studies of the Fe(Al) alloy produced two new phenomena, incommensurate spin-density-wave antiferromagnetism persisting to high temperatures and the occurrence of inverse freezing on annealing of heavily deformed Fe(40Al).

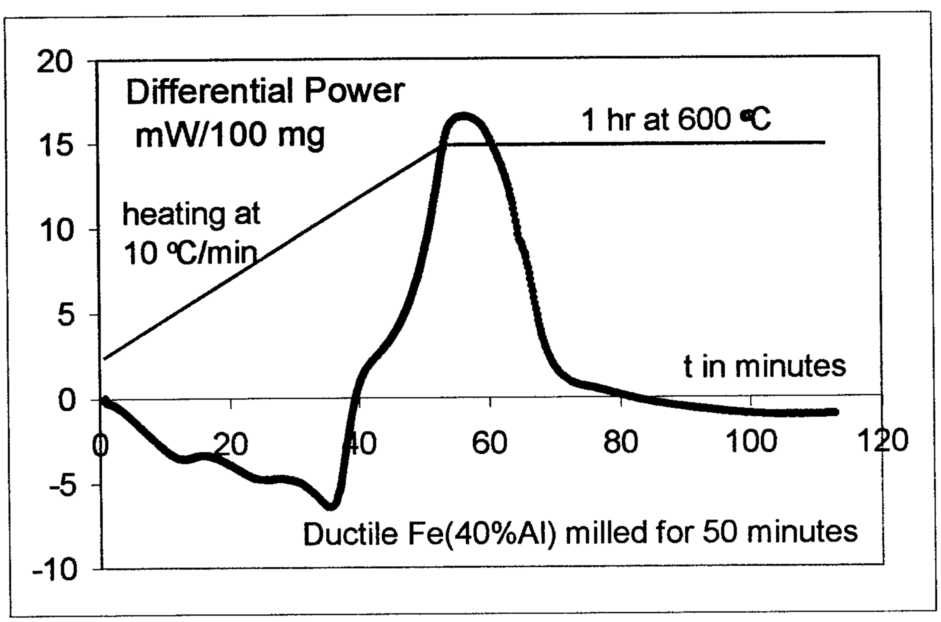


Fig. 5. Endothermic reaction on annealing mechanically milled Fe(40Al).

The ordering of the grains on heating is like going from "frozen" liquid to crystalline solid. Usually heat is given off in such a transition, that is, the reaction is exothermic. In Fe(40Al) the reaction is endothermic; see Fig. 5. Heat must be supplied, as it is when ice is melted to form a liquid. But here the "liquid" is going to the solid. Inverse freezing! It will take extensive studies of how this effect depends on alloy concentration to sort among the possible causes. Among the possibilities it could be simple thermodynamics coming from the greater lattice entropy of the CsCl structure or it may arise from changes in local alloy concentration during milling.

A report of occurrence of incommensurate spin-density waves in Fe(Al) alloys has been submitted to Physical Review Letters. As that four page document is already a summary which is difficult to make more succinct, it is reproduced here as Appendix I. We believe that spin density waves in Fe(Al) should have pervasive ramifications in condensed matter physics. The diffraction pattern is given by the wave vectors:

$$q = 2p(h \pm 1/n, k \pm 1/n, l \pm 1/n)/a_0 ,$$

where (h, k, l) are the indices of the parent bcc lattice. For each of the 12 [1,1,0] reciprocal lattice vectors there are four q's that are of almost the same length as the (1,1,0). This gives 48 spots equidistant from the origin, suitable to span the Fermi surface, producing gaps that lower the energy as shown rigorously by Overhauser for Jellium in the Hartree-Fock approximation. This discovery should lead to as many studies as have followed from the discovery of spin-density waves in chromium.

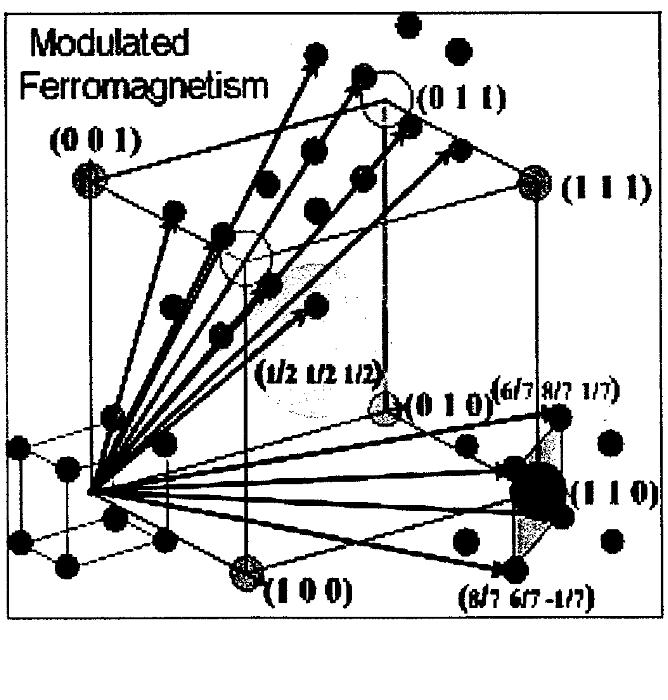


Fig. 6. Reciprocal lattice for spin density waves in Fe(40Al)

## Future directions for the iron alloys work

We intend to pursue pressing mechanically milled Hyperco with pulsed electrical heating at the asperities. Materials Modification in Fairfax, VA has developed their own technique called Plasma Pressure Compaction. We have funds for some test runs using their equipment. The solution to the compaction problem is necessary for progress in utilizing exchange softening to make Hyperco reach its full potential. It may not be sufficient, but it is, indeed, necessary for progress to achieve high-density compaction without increase in grain size.

The work on iron-aluminides has just begun. The properties of the magnetic foam will be studied in concentrations closer to FeAl to see if the grain boundaries can be more fully distinguished from the grains. The Fe(Al) magnetic phase diagram will be mapped out using magnetometry up to 1000 K.

The spin density waves in Fe(Al) are at least as interesting as those in Cr, perhaps more so because in Fe(Al) it is a modulation of ferromagnetism rather than antiferromagnetism. We plan to recruit some of the army of researchers that worked on Cr to investigate how the wave vectors depend magnetic fields, pressure, strain and on adding other elements to Fe(Al). We intend to continue the neutron diffraction, magnetometer and heat capacity experiments with the single crystals obtained from Dr. Wu at Dartmouth. We will use polarized neutrons to separate charge-density waves (atomic order) and spin-density waves (magnetic order). Can one get single-q Fe(Al)? We know nothing about the polarization vectors.

We intend to collaborate with Dr. S. Deevi at Philip Morris on the uses of the extremely well-defined polycrystalline Fe(40Al) alloys. The sensitivity of Fe(Al) to strain could be used as an information storage medium through mechanical deformation on a nanometer scale. The complex magnetic structure could be employed as a template for self-organization. The field gradient magnetometer development will continue. A permanent magnet will be used instead of the superconduction magnet for fields up to 2.5 T. The temperature control system that operates continuously from 80 K to 1050 K will be assembled. The system should be available commercially in the coming year.

The large quantities of material produced by the puck and saucer mill make the VSU facility useful for collaborations in technological applications such as magnetic refrigeration. Replacing all the commercial refrigerants with magnets seems to be a worthy goal.

## Publications

A number of publications are attached to this report as appendices. The first is the paper on spin-density waves in iron-aluminum alloys, which has been submitted to Physical Review. In addition several papers authored or co-authored by Noakes and/or Stronach on muon spin rotation studies of various materials (primarily materials exhibiting one or another form of exotic magnetism, or an interplay of magnetic ordering and superconductivity) are included.

Noakes was chief editor of the *Proceedings of the Ninth International Conference on Muon Spin Rotation*, which was held in Williamsburg, VA in June 2002. The title page of this book is included as an appendix.

## Student Participation

Two graduate students have taken part in this program and have received financial support. Matthew Belk has been working on the neutron scattering studies of Fe(Al) alloys and is a co-author of the paper submitted to Physical Review Letters on this topic. He is a recipient of a Defense Department Fellowship, which provides his financial support. We anticipate that he will complete his M.S. thesis and degree in May 2004.

Terry Clarke is working on the development of the gradient-field magnetometer, and we anticipate completion of his M.S. thesis and degree in May 2004 as well. Mr. Clarke holds a full-time position as Associate Professor of Physics at Southside Virginia Community College, and has been working on his M.S. degree part-time at VSU for several years.

Two other graduate students, Bryan Kessler and Daniel Dotse, are working on the related micromagnetics research program. Yet another graduate student, Pamela Bowman, is new to the program and hasn't yet chosen a thesis topic. An undergraduate senior physics major, Luisa Soaterna, is also doing research with Drs. Noakes and

Stronach, analyzing μSR data on high-temperature superconductors. She is a recipient of a Defense Department Scholarship.