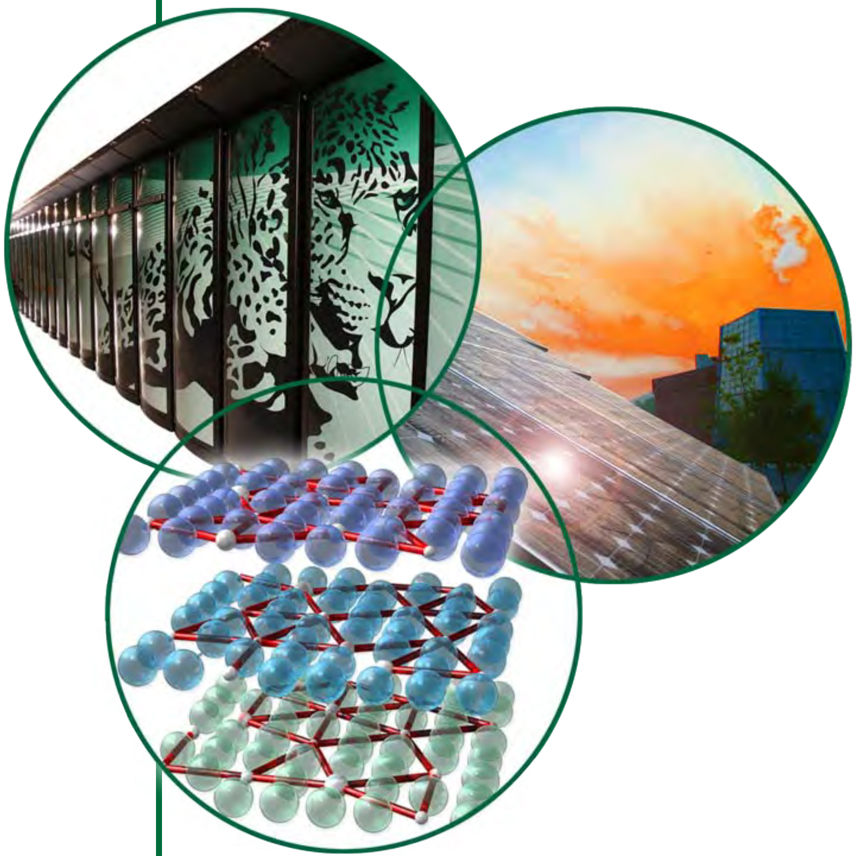
Project ID: LM043

Nanostructure, Chemistry and Crystallography of Iron Nitride Magnetic Materials by Ultra-High-Resolution Electron Microscopy and Related Methods



DOE 2011 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

Lawrence F. Allard
HTML User Program
Materials Science and Technology Division
Oak Ridge National Laboratory

Washington, DC
May 12, 2011

Sponsored by
U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies

U.S. DEPARTMENT OF ENERGY

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The HTML User Program: Background

- The HTML is a National User Facility that supports the missions of DOE, EERE and the Vehicle Technologies Program in particular, by working with industry, universities, and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum. The HTML is organized into six user centers, which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization.
- Access to the HTML User Program is provided through the HTML User Program proposal process. Research proposals are reviewed by a committee and approved based on scientific merit, relevance of the proposed research to the mission of DOE's Vehicle Technologies Program, feasibility, and non-competition with the private sector. Projects have a well-defined scope, and research is completed within 24 months and often involves multiple user visits to the HTML.
- Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, and users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature. A nonproprietary project is complete when research ends, accompanied by the required publication in the open literature and/or presentation at a professional conference. For proprietary research, the user owns the research data, and all costs at the HTML are paid by the user based on DOE guidelines for ORNL cost recovery.

The HTML User Program – FY2010 Activity

During FY2010, the HTML User Program collaborated with 18 companies, 25 universities, and 6 national laboratories on 68 user projects addressing critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program. There were 96 researchers, 63% of them first-time users, who visited the HTML for a total of 716 research days.

The HTML User Program FY2010 budget was $5,312,400 and allocated as follows:

- Capital equipment: $881,959
- Operations: $4,430,441

Users cost-share their HTML user projects through:

1) direct involvement with HTML staff members during the development of the user project;
2) funding their time and travel to the HTML to perform research;
3) cost of materials provided by the user or the research performed prior to the user project;
4) collaboration with HTML staff members to analyze the data and publish the results.

The HTML also supports the education and preparation of the next generation of scientists and engineers. During FY2010, students and professors from 25 universities participated in the HTML User Program. Five of those students earned their Ph.D. degree and one earned her M.S. degree based in part on research they conducted through the HTML User Program.

Relevance of HTML User Program Activities to the VT Program

- The Vehicle Technologies Program funds the operation of the HTML User Program to maintain world-class expertise and instrumentation capabilities for materials characterization to work with industry, universities and national laboratories toward the goals of the Vehicle Technologies Program. The HTML User Program capabilities at the Oak Ridge National Laboratory support the activities of the Vehicle Technologies Program's subprograms in Lightweight Materials, Propulsion Materials, Energy Storage, Solid State Energy Conversion, Combustion & Emissions Controls, Power Electronics & Electric Motors, and Non-Petroleum Fuels.
- During FY2010, the HTML User Program managed **14** characterization projects relevant to the Vehicle Technologies Program's technology areas of Energy Storage and Power Electronics & Electric Motors. This poster presentation highlights ***one*** of these user projects.
- The user project with the University of Minnesota highlighted in this poster presentation addresses the need for developing magnets that do not contain rare earth minerals.

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials"

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Timeline

- Start date: 4/30/10
- End date: 5/1/12
- % complete: 90%

Barriers

- Rare Earth Minerals

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Collaborators

- **Users:** Jian-Ping Wang and Nian Ji, University of Minnesota
- **HTML Staff:** Lawrence F. Allard, Harry M. Meyer III and Edgar Lara-Curzio

Project ID: LM043_Allard_2011

Collaborations

As a DOE User Facility, the HTML User Program is collaborative in nature. Potential users are assisted with the proposal submission process as necessary, and all research is hands-on with direct involvement from both user and HTML User Program staff researchers. The DOE-required publication of results for non-proprietary projects is also a collaborative effort.

Collaborators on the user project reported in this presentation:

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__University of Minnesota__
Jian-Ping Wang and Nian Ji

html
HIGH TEMPERATURE MATERIALS LABORATORY

__HTML User Program__
Lawrence F. Allard, Harry M. Meyer III, Edgar Lara-Curzio

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials"

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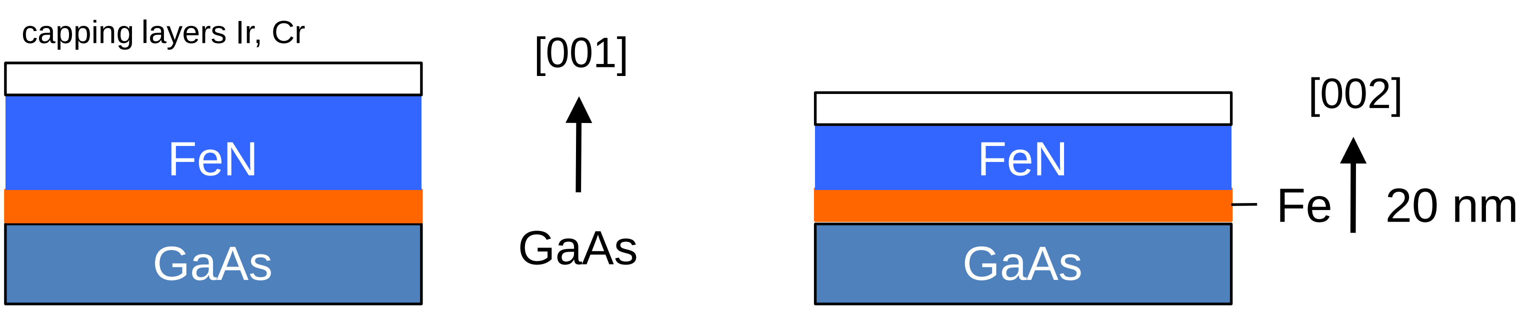
Overview, Objective and Relevance

- Widespread deployment of hybrid-electric and battery electric vehicles may increase worldwide demand for rare earth elements and certain other materials. It is likely that future supply of these materials may not be able to meet the demand from these technologies[1].
- Attaining the levels of cost reduction required to meet 2015 and 2020 motor cost targets (50% to 75%) requires considering new materials for all components in the motor (e.g., soft magnetic core materials)[2].
- $Fe_{16}N_2$ is a metastable phase that exhibits the highest saturation magnetization value ever reported.
- The objective of this user project with the University of Minnesota is to characterize the microstructure and chemical composition of $Fe_{16}N_2$ thin films at the atomic level. Such information will enable the development of strategies for synthesizing larger volumes of this material for potential applications in hybrid-electric and battery electric vehicles.

1.- *Critical Materials Strategy*, U.S. Department of Energy, December 2010.
2.- *Multi-Year Program Plan 2011-2015*, DOE Vehicle Technologies Program. December 2010

Two thin film Fe-N samples were prepared by "facing target sputtering" onto GaAs substrates at the University of Minnesota:



sample -0412

thickness of FeN layer ~50nm

sample-0510

thickness of FeN layer ~36nm

Note: imaging and diffraction results were similar for both sample sets; in the following slides, imaging results from sample -0412 and electron diffraction results from sample -0510 are presented.

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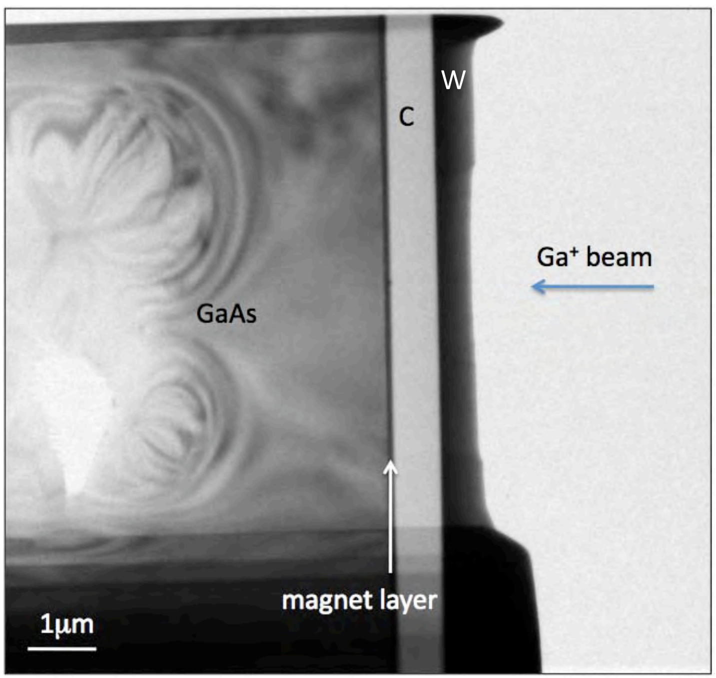
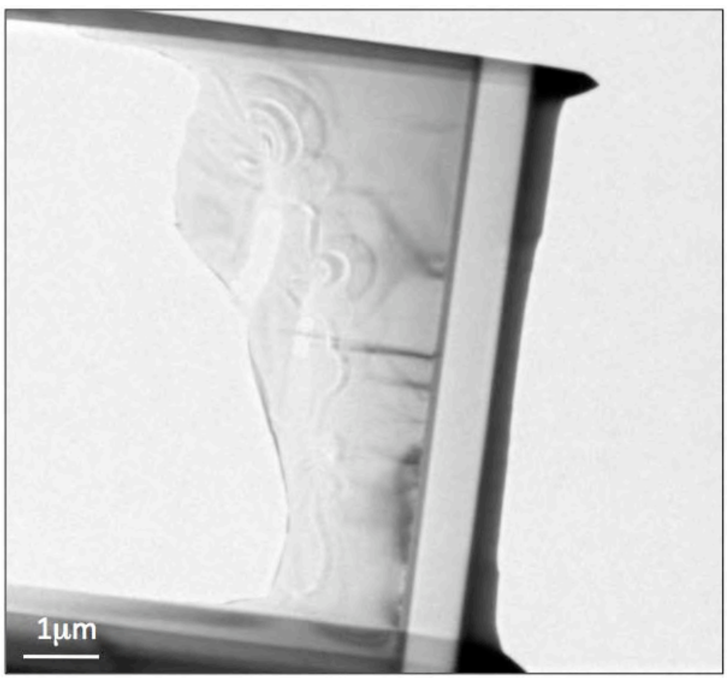
Electron microscopy specimen preparation:

- Focused-Ion-Beam (FIB) milling was used to make electron-transparent thin sections with GaAs[110] normal (electron beam direction).
- FIB samples coated with 700nm carbon (C) followed by a 2-μm thick tungsten (W) layer to protect surface.
- Post-FIB milling with "Nanomill" uses Ar ion beam to make final thin specimens.



Initial FIB section



After Nanomill

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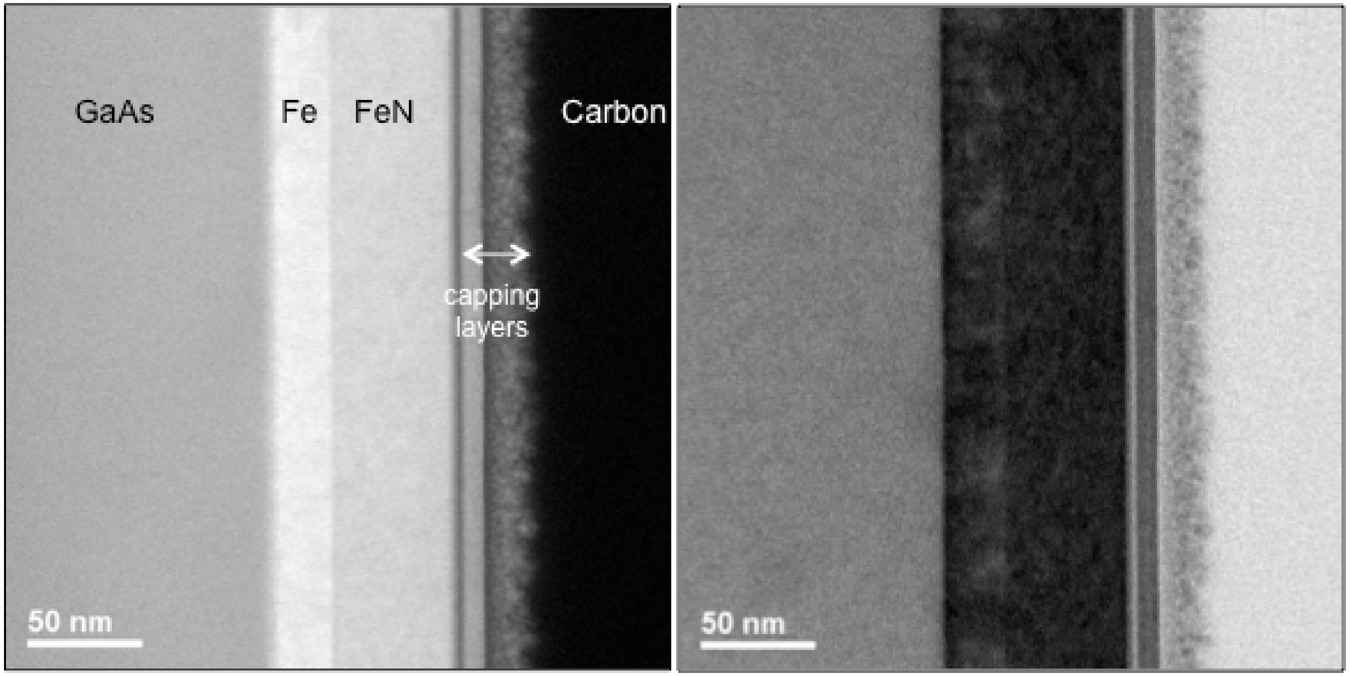
high-angle annular dark-field



bright field

- Aberration-corrected scanning TEM imaging using a JEOL 2200FS at the High Temperature Materials Laboratory.
- High-angle annular dark-field (HAADF) and bright-field (BF) images acquired simultaneously.
- HAADF images show brighter contrast for higher average atomic number regions (e.g. Fe is brighter than FeN).

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Chemistry of Sample -0412

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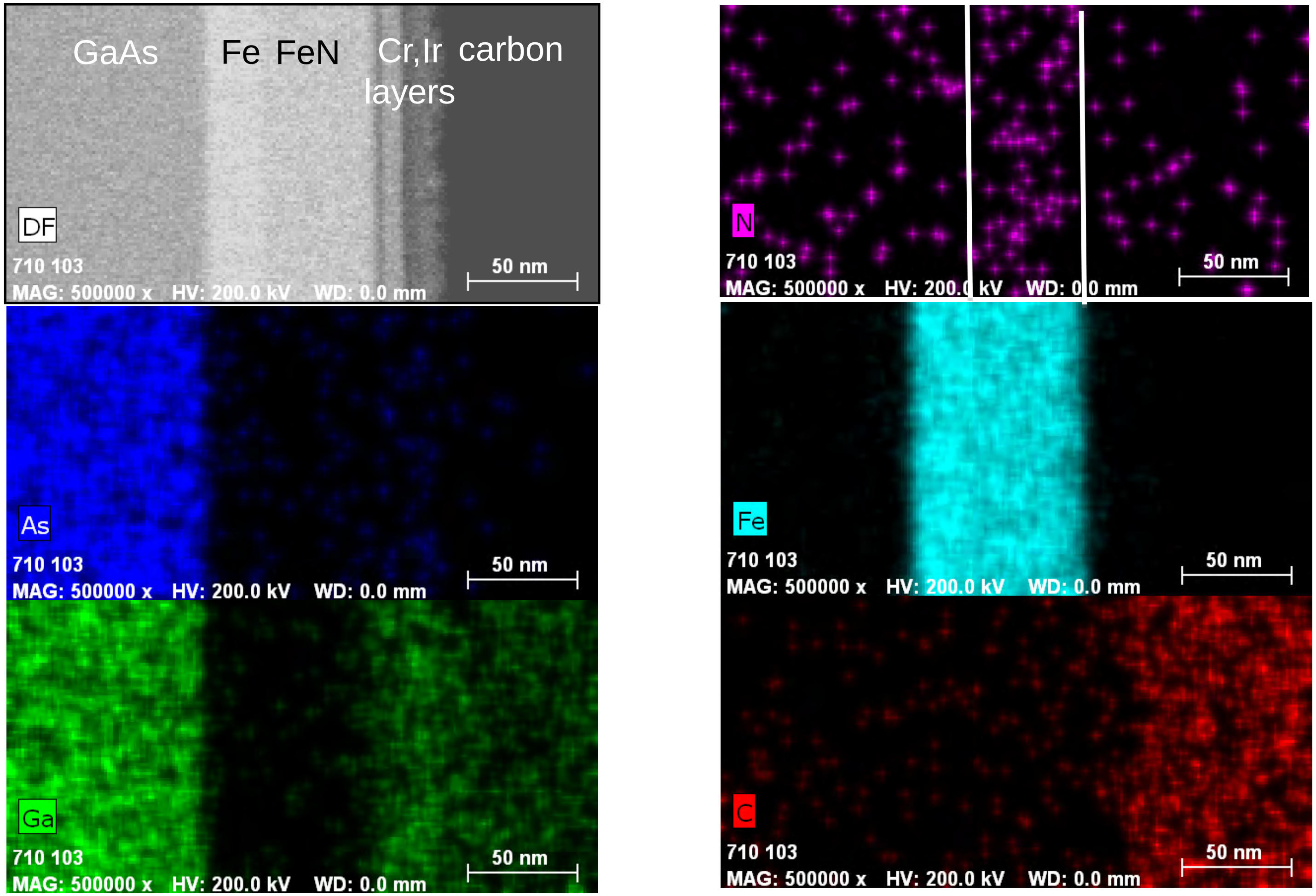

The Fe/FeN layers are consistent with a decrease in Fe intensity and an increase in N intensity in FeN, due to the presence of N in the layer.

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Chemistry of Sample -0510

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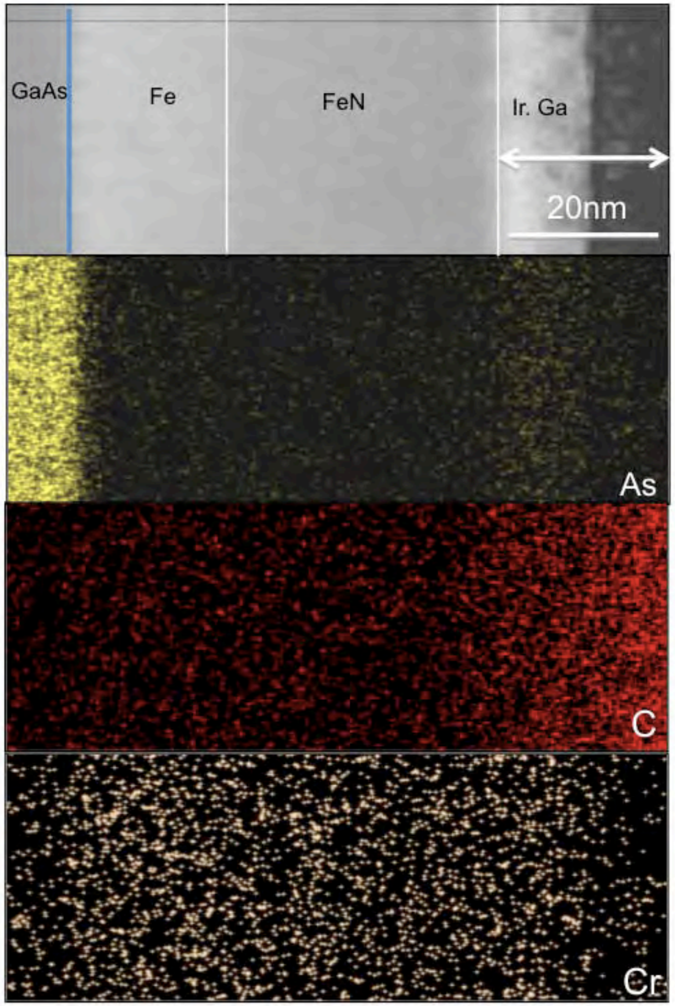

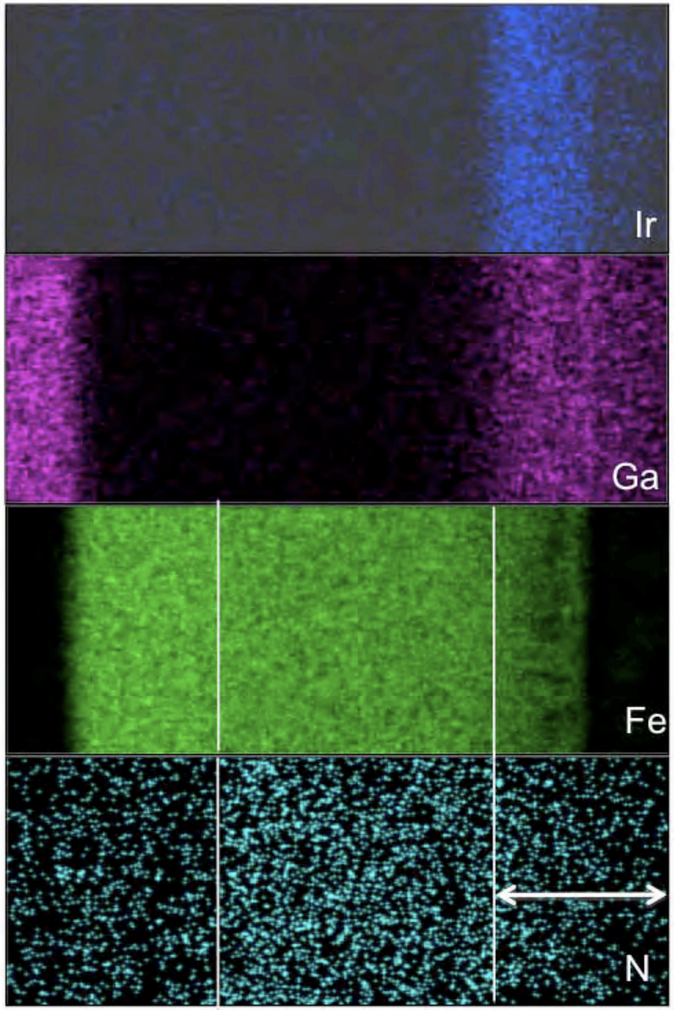

Note: Ir layer has Ga imbedded from FIB process

Arrow ⟷ locates FeN surface in x-ray maps

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Crystallographic structure

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- α–Fe is body-centered cubic, with lattice parameter 2.8665Å.
- Addition of N at up to 1N per 8Fe pushes the structure to tetragonal, α'-Fe_8N, with about double the Fe cell size in x, y and z, and having lattice parameters of a = 5.72Å, c = 6.29Å. The N atoms populate a small fraction of the octahedral sites *randomly*.
- With heat treatment, α'-Fe_8N transforms into α''-$Fe_{16}N_2$, and N atoms become ordered at the ideal composition in $1/24^{th}$ of the octahedral sites to produce ordering reflections in electron diffraction. Lattice parameters and space group (I4/mmm) remain the same.
- The (001) surface of GaAs is a close match crystallographically with the (002) surface of α-Fe, and therefore is an excellent substrate for growing α-Fe as a seed layer to be nitrided during growth of the FeN layer, since (the Fe lattice in) α''-$Fe_{16}N_2$ closely matches the lattice of α-Fe.

University of Minnesota User Project: “Characterization of Iron Nitride Magnetic Materials” Structure of Sample -0412

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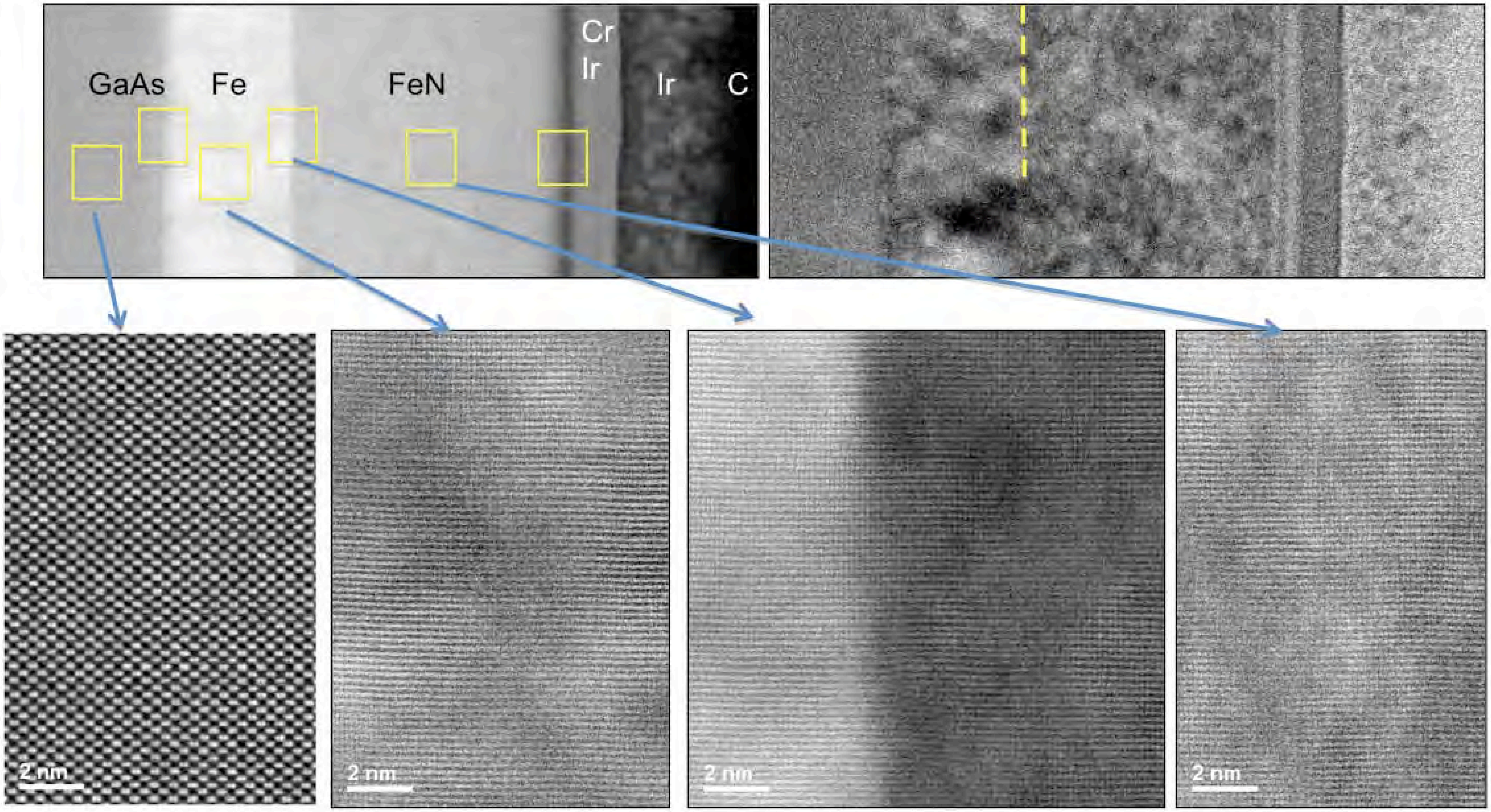

HAADF imaging of sample-0412. 10Mx direct magnification

University of Minnesota User Project: “Characterization of Iron Nitride Magnetic Materials” Chemistry of Sample -0412

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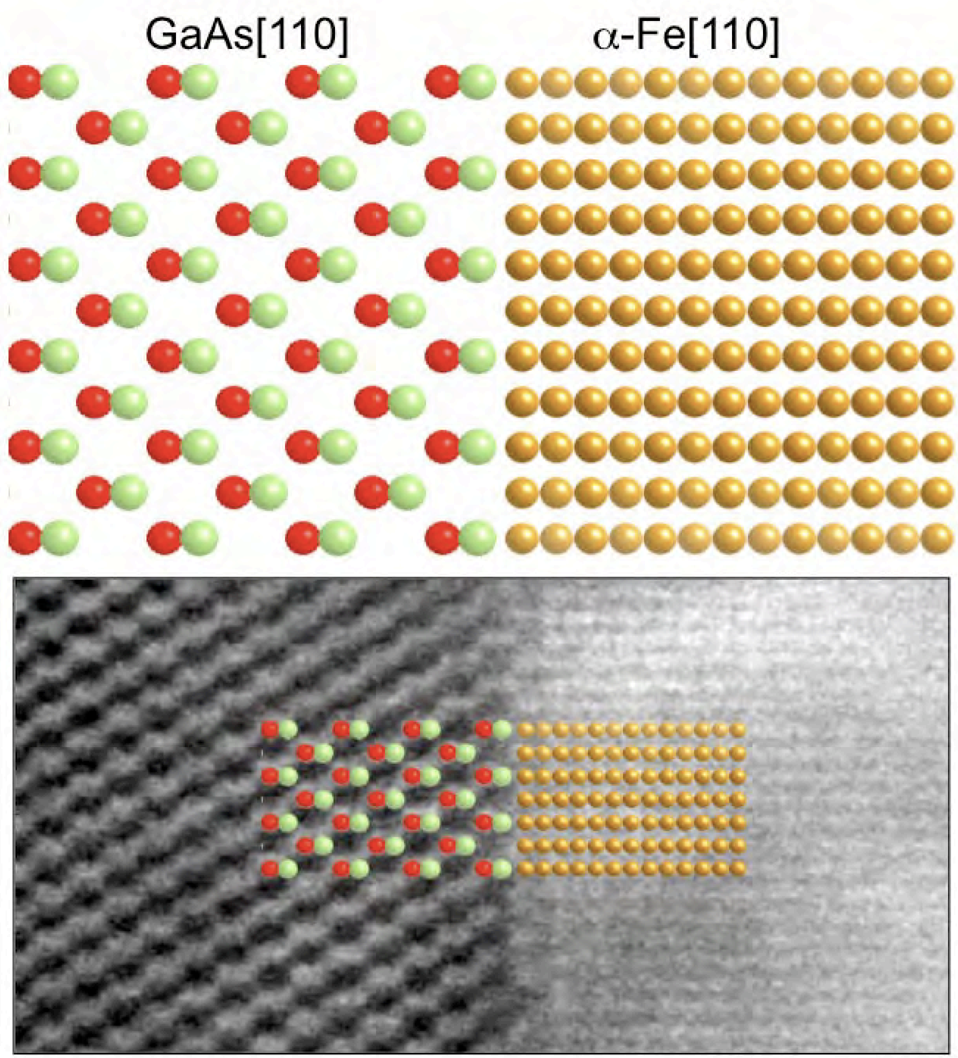

HAADF image shows nearly perfect coherence between Fe and GaAs lattices, and nearly a monoatomic interface structure.

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Structure of Sample -0412

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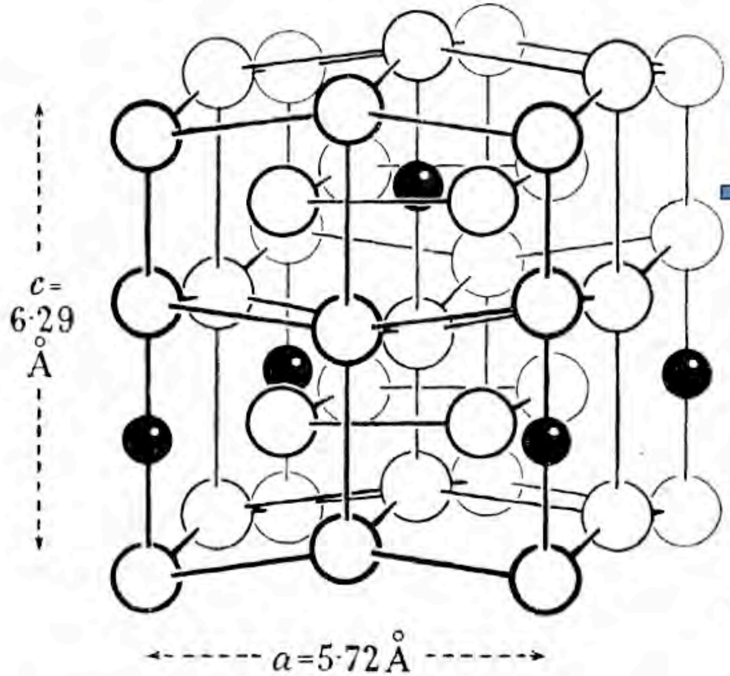
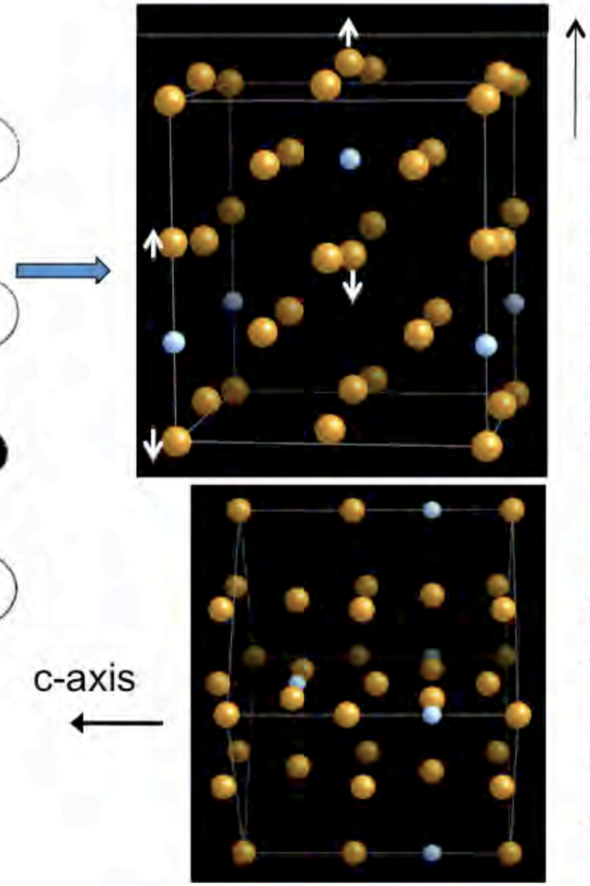
Structure of α"-$Fe_{16}N_2$



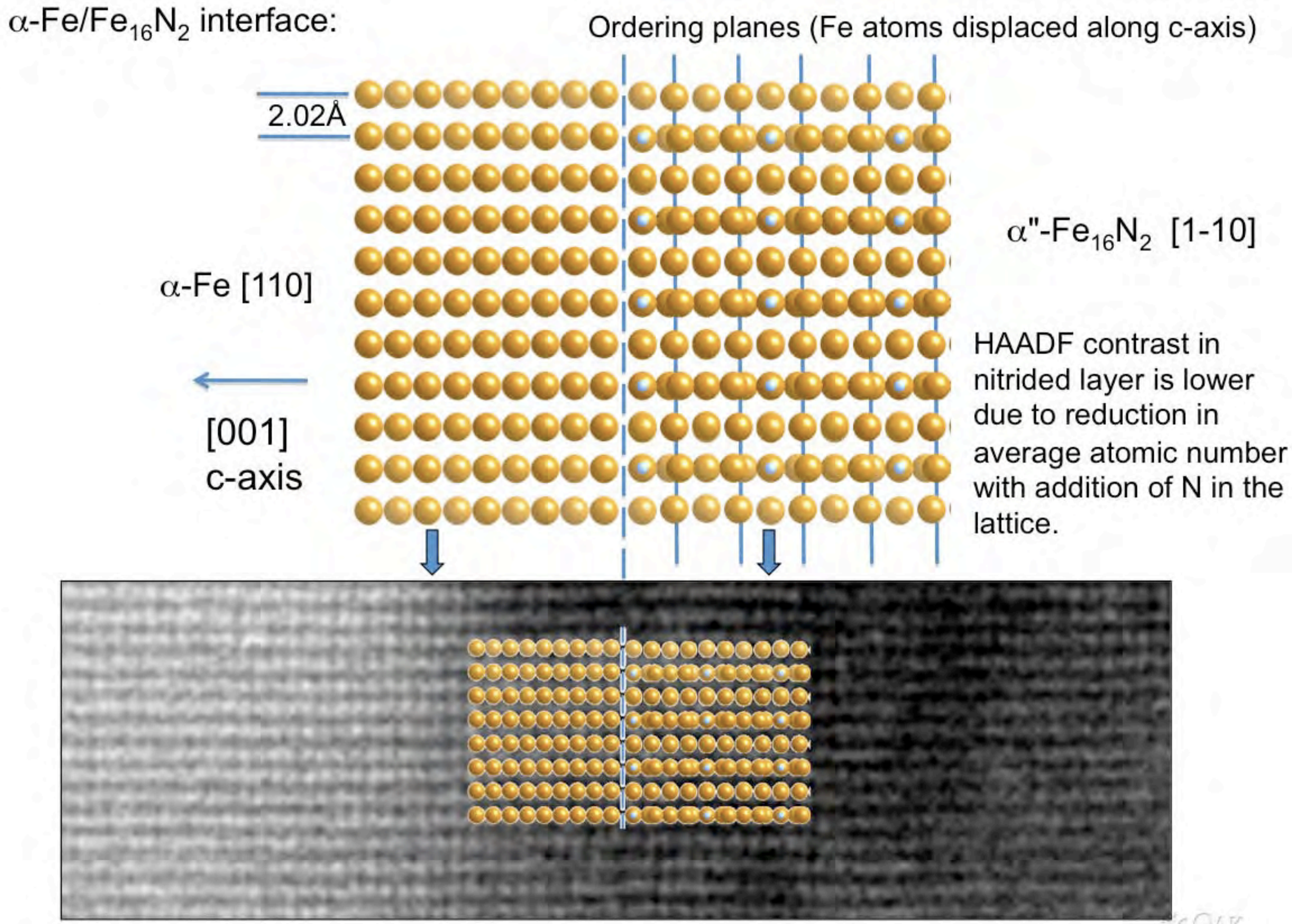
Original model of Jack (1951)



Nitrogen atoms ordered in octahedral sites cause shift in Fe atoms along the c-axis.

- K. H. Jack, Proceedings of the Royal Society of London. Series A, **208**, No. 1093 (1951), pp. 200-215
- H. Sawada et al., Phys. Rev. B **50**, 10004-10008 (1994)

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Structure of Sample -0412



University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Electron Diffraction Analysis

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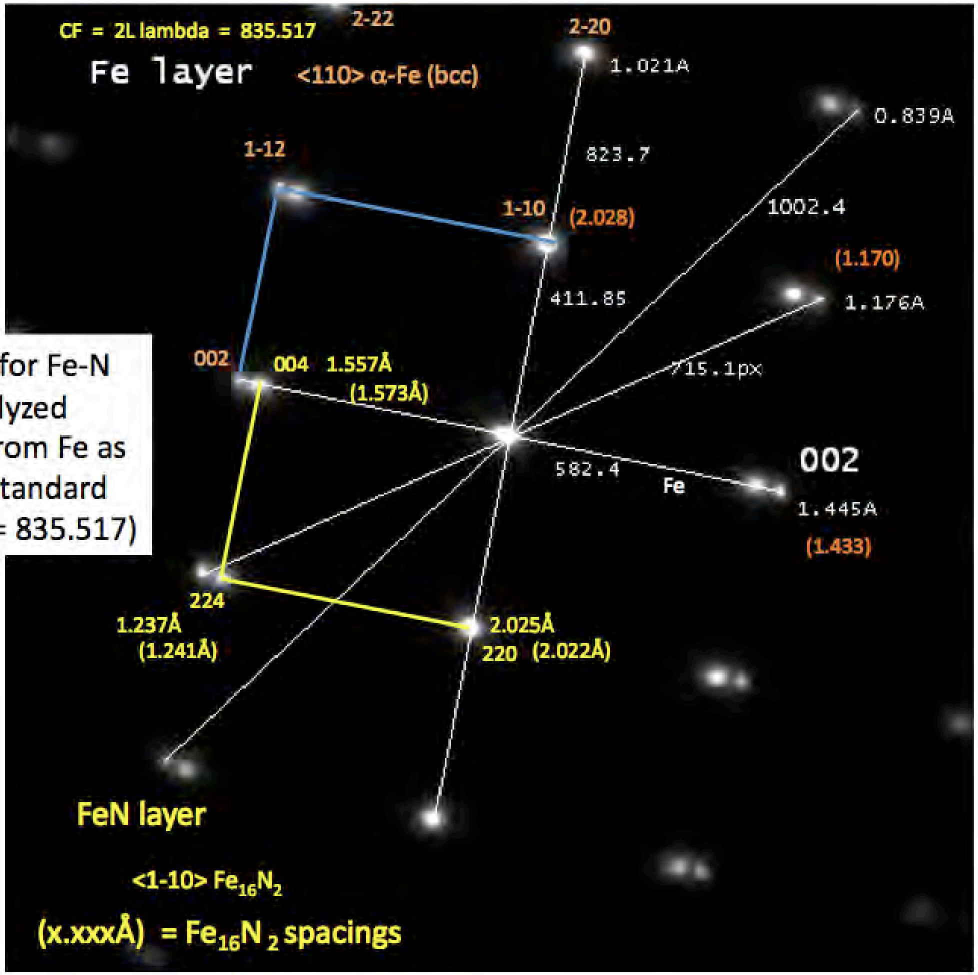
Combined results for Fe + FeN layers:

Spacings for Fe-N layer analyzed with CF from Fe as internal standard (new CF = 835.517)



CF = "camera factor"

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" Electron Diffraction Analysis

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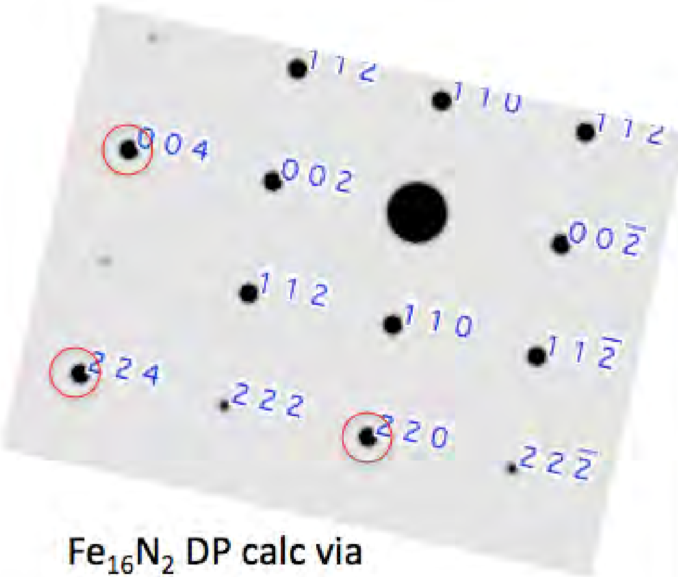
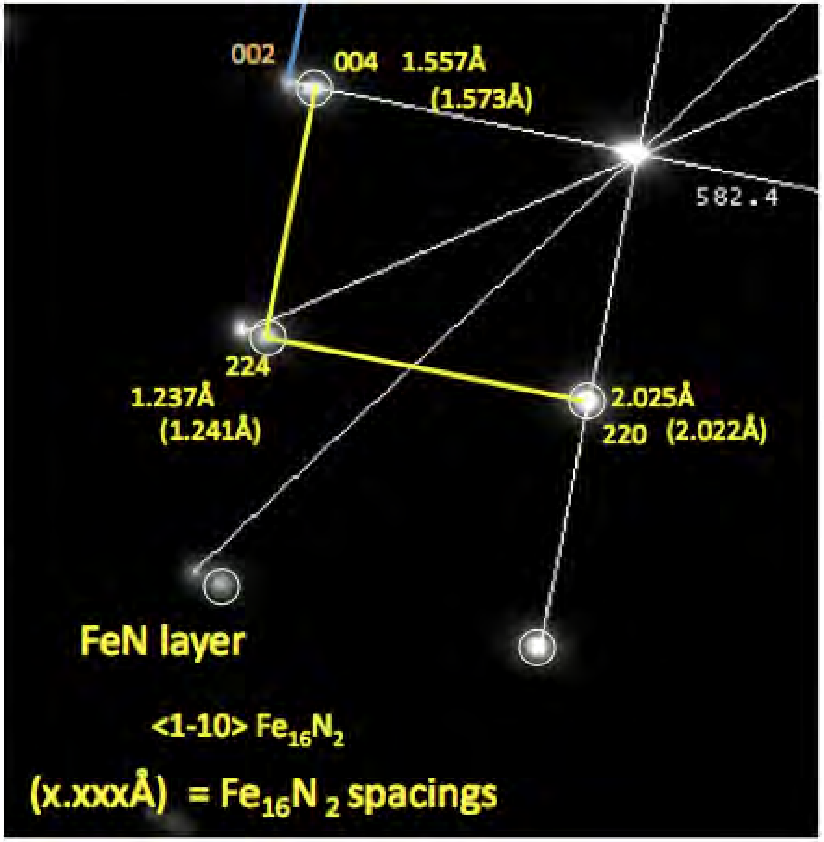


$Fe_{16}N_2$ DP calc via SingleCrystal



The reflections circled in the experimental electron diffraction pattern match closely the same index reflections for $Fe_{16}N_2$ in the computed pattern. The remaining computed reflections <u>do not</u> appear in the (nominal) $Fe_{16}N_2$ pattern.

University of Minnesota User Project: “Characterization of Iron Nitride Magnetic Materials” Electron Diffraction Analysis

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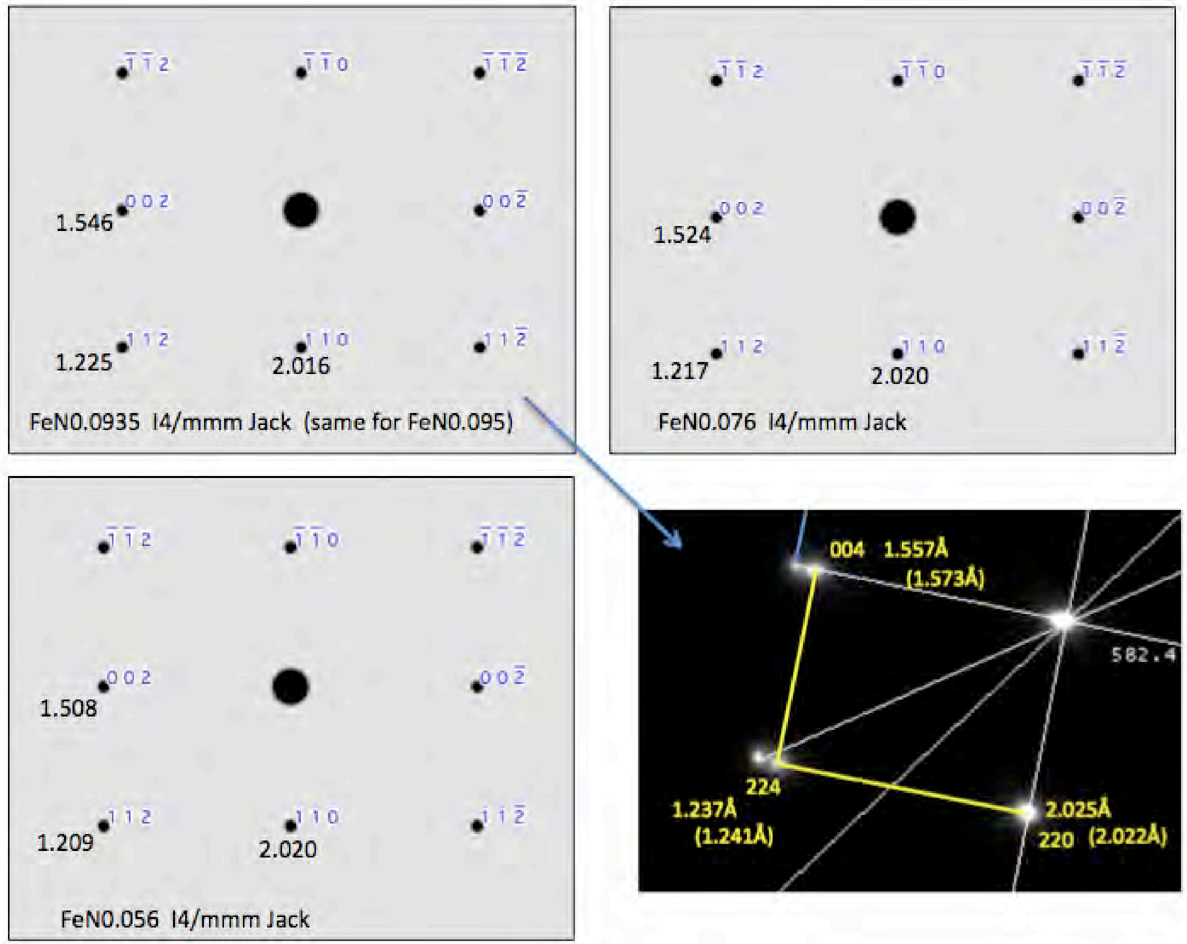
Jack (1951) studied a series of "nitrogen-deficient" FeN compounds, all with the I4/mmm (tetragonal) space group, with nearly the same lattice parameters as ordered a"-$Fe_{16}N_2$. Our precise measurements are consistent with the major component of the FeN layer being a nitrogen-deficient disordered structure.

$FeN_{0.095}$ $FeN_{0.076}$



$FeN_{0.056}$

K. H. Jack, Proceedings of the Royal Society of London. Series A, **208**, No. 1093 (1951), pp. 200-215

University of Minnesota User Project: "Characterization of Iron Nitride Magnetic Materials" X-ray Photoelectron Spectroscopy

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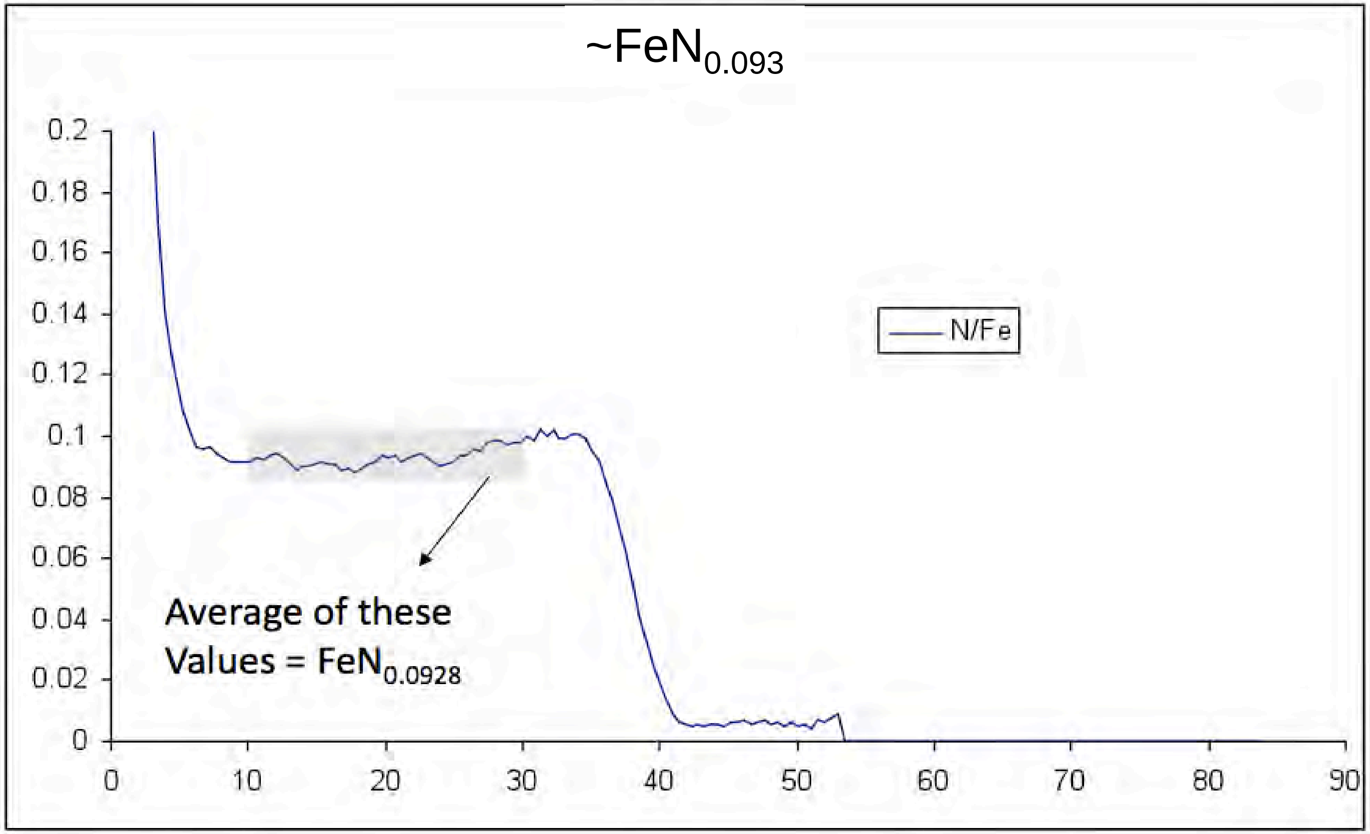

The N/Fe ratio in an XPS depth profile through the 36-nm thick FeN layer of sample-0510 shows a concentration of N lower than the ideal N/Fe of 0.125 as expected for the α''-$Fe_{16}N_2$ compound.

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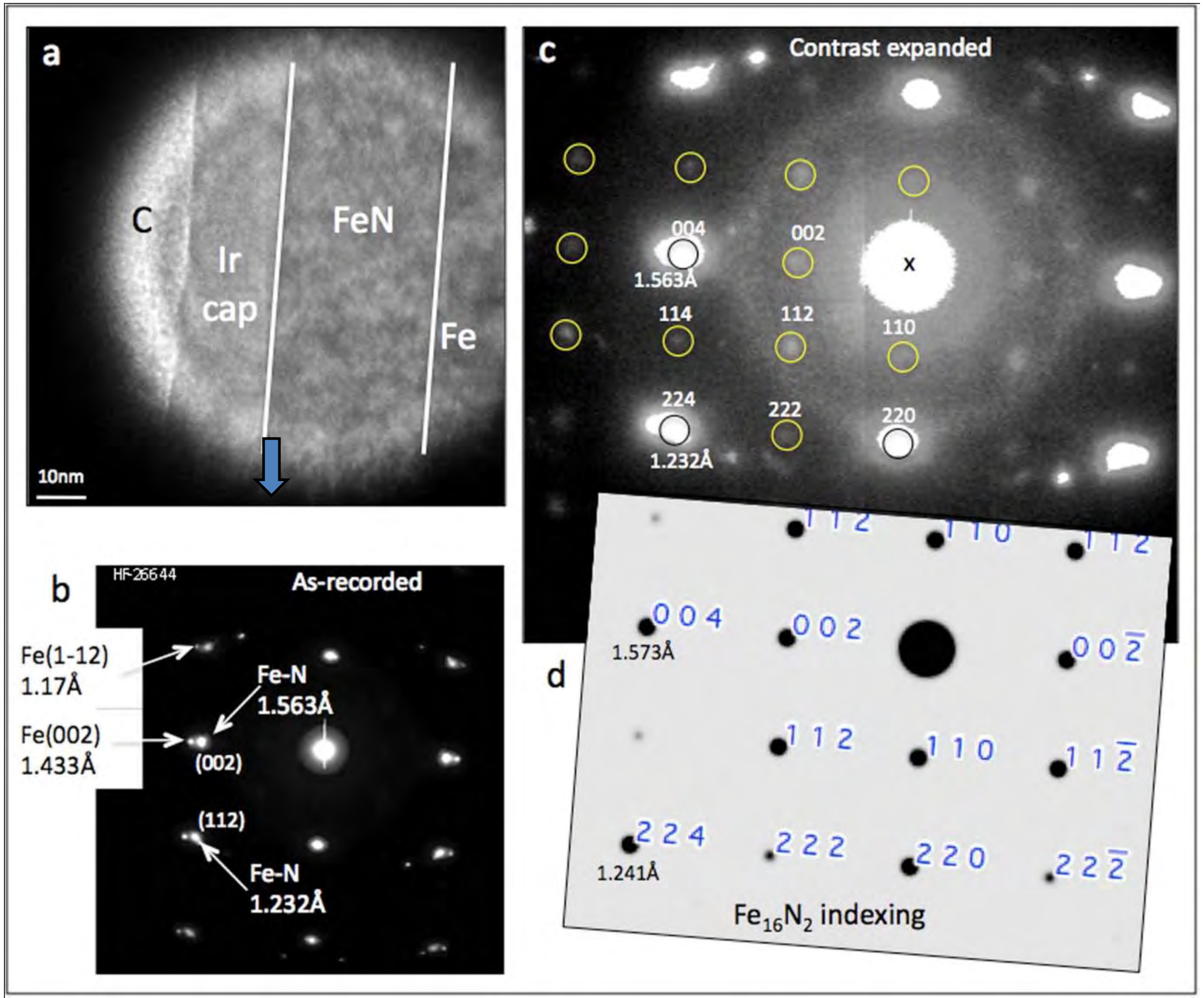
Sample-0510

Microarea electron diffraction pattern from Fe + FeN layers (with some overlap) matches prior slide; but with contrast expanded (as in c), a periodic net of reflections (circled) consistent with the ordering reflections of $Fe_{16}N_2$ is evident.

This result clearly shows the presence of a fractional composition of $Fe_{16}N_2$ in the nitrided layer.



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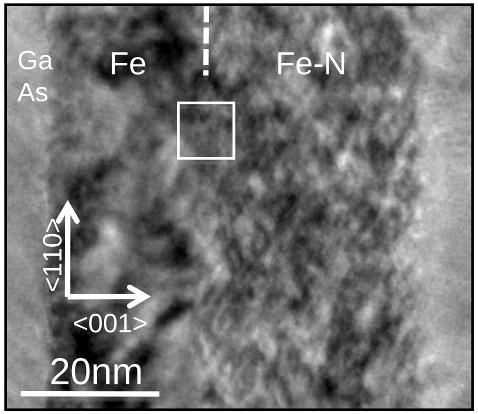
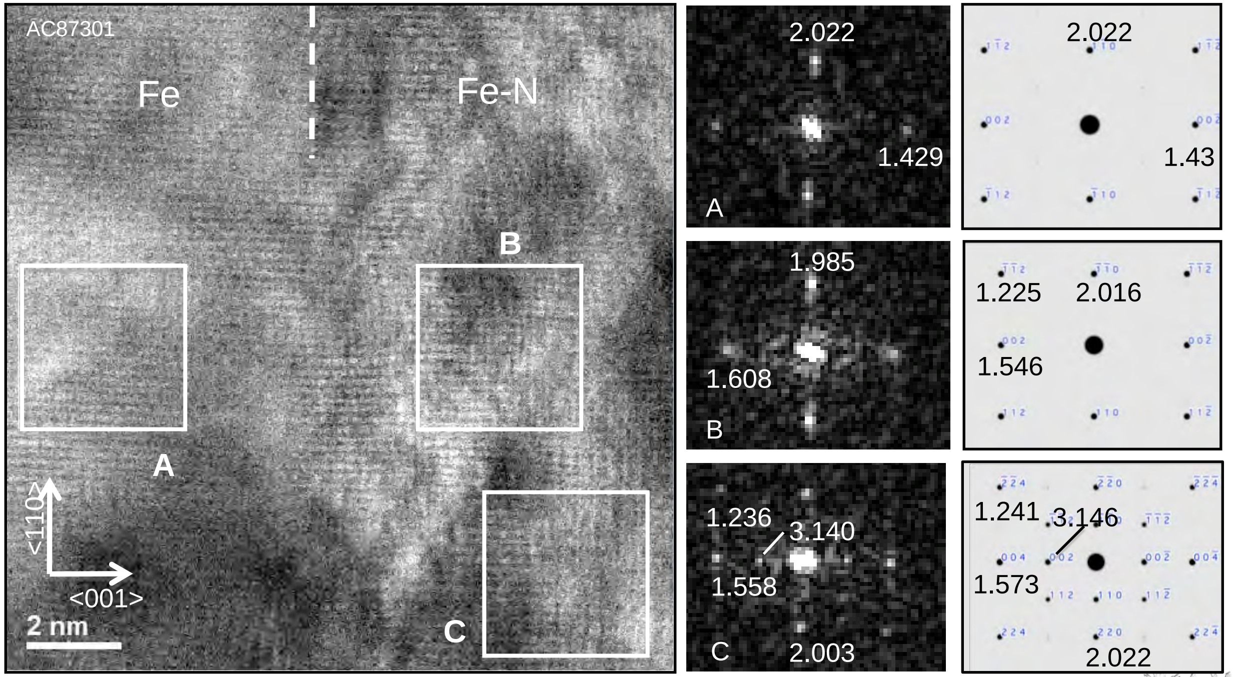


Diffractogram analysis of aberration- corrected STEM images:

- BF STEM image at Fe-FeN interface chosen for best low-noise diffractograms
- Diffractogram from "A" in Fe layer used for calibration of FeN layer
- "B" shows typical disordered region, but "C" shows ordering spots suggesting $Fe_{16}N_2$.



Project ID: LM043_Allard_2011

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Summary

- The University of Minnesota was able to take advantage of a wide array of materials characterization capabilities available through the HTML User Program, which maintains world-class expertise and unique instrumentation gathered in one convenient location. The University of Minnesota characterized the microstructure, atomic arrangement, and composition of iron nitride thin films.
- Using aberration-corrected scanning electron microscopy and electron diffraction techniques, it was possible to identify the phases present in these films, their distribution and their crystallographic structure.
- The chemical composition of the films was determined by X-ray photoelectron spectroscopy and EDS. The combination of XPS and STEM results allowed verification of the presence of domains of $Fe_{16}N_2$, which has the highest saturation magnetization value ever reported.
- These results will enable the development of processing strategies for producing iron nitride materials with a high concentration of the metastable phase $Fe_{16}N_2$. The development of iron nitride magnets addresses an important barrier associated with the use of rare earth minerals in magnetic materials for multiple automotive components (e.g., electric motors).