



THE Ames Laboratory
Creating Materials & Energy Solutions

FY2015 LDRD Annual Report

Laboratory Directed
Research and Development
Program Activities

Office of the Director
January 2016



Ames Laboratory is a U.S. Department of Energy
Laboratory managed by Iowa State University

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ABOUT AMES LABORATORY

Ames is a U.S. Department of Energy Laboratory managed by Iowa State University under contract DE-AC02-07CH11358.

The Laboratory's main administration facilities are at 311 TASF on the campus of Iowa State University.

For more information about Ames Lab and its pioneering science and technology programs, see www.ameslab.gov.

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I am pleased to submit the Ames Laboratory's Annual Report on its Laboratory Directed Research & Development (LDRD) activities for fiscal year 2015 (FY2015), a program inaugurated midyear in FY2013. The LDRD funds enable creative and innovative R&D projects at Ames Laboratory (AMES) that directly support our mission and initiatives. Selection of projects is the responsibility of the Laboratory Director, with each project identified as strategic in nature and reflects scientific quality, innovativeness, and value to mission-related initiatives.



LDRD is an invaluable resource that permits us to anticipate, and prepare to contribute to, the future science and technology needs of the Department of Energy (DOE) and the nation. The LDRD program objectives are to stimulate innovation and creativity, and to enhance the research activities to keep the Ames Laboratory at the forefront of science and technology. LDRD funding will continuously refresh the Laboratory's scientific and technological vitality, and enable AMES to respond to emerging R&D opportunities of clear potential benefit to DOE's mission. The program enhances AMES' ability to attract and retain the high-caliber scientists and engineers essential to pursue the mission of DOE and the needs of the nation. The LDRD program helps insure that AMES will continue providing scientific and technical leadership in its mission areas.

I can attest that in managing the AMES' LDRD Program, we have adhered without exception to the requirements of DOE *Order 413.2c* and associated guidelines. Our program management continually strives to be more efficient. In addition to meeting all reporting requirements, our LDRD Program Office continues to implement improvements that better serve all LDRD stakeholders, from our researchers, managers, budget office, to our DOE Site Office colleagues.

The individual project reports that follow demonstrate the AMES' researchers have pursued projects at the forefront of their respective fields and have contributed significantly to the advancement of our major initiatives. Evidence of the strength of the program is found from the contributions to significant aspects of the laboratory's Strategic Plan, with future evidence anticipated through follow-on sponsorship and technology transfer.

Adam Schwartz
Director, Ames Laboratory

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Acknowledgements

AMES’ LDRD Program Office comprises the Chief Research Officer, Dr. Duane D. Johnson, Associate Laboratory Director for Sponsored Research, Deb Covey, and LDRD Program Administrative Specialist, Lisa Rodgers. The program reports to the Laboratory Director, Dr. Adam Schwartz, through the Chief Research Officer. The LDRD program’s management is grateful for the critical support received throughout the year – from the division’s business offices and lab budget office. Special appreciation is due to the many experts who proposed and perform the research and provide the project reports; to the technical and administrative management of AMES’ programs and divisions in which the R&D is pursued; to those experts throughout the DOE complex who provide anonymous peer review for LDRD proposals; and to the leaders in the laboratory’s strategic initiative areas, whose vision and understanding of the nation’s technological needs guide and refine the content of AMES’ LDRD portfolio.

Research Reports – by Component

Within a given LDRD Components (Lab Strategic Initiatives, Novel Projects, or Exceptional Opportunities), the projects are list by [LDRD Number], (Strategic/Mission Area) and TITLE.

Novel Projects

[2013-GOR-1218] (*Cybersecurity;Applied Math*) **Dynamic Whitelist Generation for Automated Intrusion Prevention** (6/10/13 to 9/30/14, extended to 9/30/2015) 10

Strategic Initiatives

– *Materials at the Edge of Stability (EdgeS) – new in 2015, replacing MADD Science*

[2014-LOG-1212] (*Basic Science and Energy Security*) **Self-Healing Adaptive Structural Coatings** (12/15/13 to 9/30/2015 – Cancelled in FY15, PI left lab) 11

[2015-JCUI-2008] (*Basic Science and Energy Security*) **Improving Ductility of High Si Electrical Steel** (8/25/15 to 9/30/2016 – Late Start) 12

[2016-MTAN-0815] (*Basic Science & Energy Security*) **Novel modular thermal conductivity measurement setup** (8/25/15 to 9/30/2016 – Late Start) 13

[2016-RPRO-0815] (*Basic Science & Energy Security*) **Frequency-domain magnetic susceptometer for pressure and ultra-low temperature** (8/25/15 to 9/30/2016 – Late Start) 14

– *Greener Advances in Catalysis for Energy (GrACE)*

[2014-SLO-0802] (*Basic Science & Energy Security*) **Customized Assembly of Catalytic Systems by 3D Printing Technology** (12/15/13 to 9/30/2015) 15

[2014-LWA-0413] (*Basic Science & Energy Security*) **Adsorption-induced Shape-changing in Nanoalloys: Extended Alloy Wulff Construction with First-principles Calculations** (12/15/13 to 9/30/2015) 16

– *Solid-State NMR Sciences (PRIMROSE)*

[2014-SAD-0709] (*Basic Science & Energy Security*) **Sensitizers for Dynamic Nuclear Polarization NMR Spectroscopy** (12/15/13 to 9/30/2016) 17

[2015-MPRU-0812] (*Basic Science & Energy Security*) **Studies of Novel Materials using Dynamic Nuclear Polarization NMR Spectroscopy** (1/1/15 to 9/30/2017) 18

[2015-VDOB-0909] (*Basic Science & Energy Security*) **Theory and Simulation of Solid-State NMR for Characterization of New Materials** (10/1/14 to 9/30/2015) 19

Exceptional Opportunities

– *2015 Spedding Fellowship awarded to Dr. Frédéric Perras to support Solid-State Dynamical Nuclear Polarization NMR Science (see Solid-State NMR Science)*

LDRD Objectives

The objectives of AMES' LDRD portfolio are to enhance the Laboratory's ability to achieve its mission by enabling selected critical projects for which no other source of funds is available. LDRD funds will be used: (1) to foster innovation and creativity from the scientific and technical staff by supporting their pursuit of novel, forefront science and technology research ideas, new concepts, and high-risk/high-reward research and development projects; (2) to develop, recruit, and retain the researchers needed to maintain and enhance the scientific, engineering, and technical vitality and capabilities of the Laboratory; (3) to exploit the technical potential of the Laboratory for the benefit of the nation; and (4) to enable the Laboratory's R&D planning by supporting its mission and strategic plans, as described in its Strategic and Lab Plans.

LDRD Components

The program provides support for *Initiatives, Novel Projects, and Exceptional Opportunities*.

Strategic Initiatives are employee-initiated proposals that address at least one of the strategic goals or an area of potential growth within AMES' Strategic Initiatives.

The **Strategic Initiatives** are as follows:

- Materials Discovery and Design (MaDD) Science
- Greener Advances in Catalysis and Energy (GrACE)
- Primary Research Initiative on Magnetic Resonance of Solid-state for Energy (PRIMROSE)

Novel Projects are a balance of basic, applied, single-investigator, and multidisciplinary projects in new areas or directions, not necessarily in direct support of our initiatives.

Exceptional Opportunities is an integral part of the pursuit of capabilities in a strategic area that enhances human and physical resources to support that area. This component consists of projects that do not fit neatly into the other two or that can arise outside the normal fiscal-year schedule, e.g., strategic hires, collaborations with external institutions where a superior expertise resides, or projects offering exceptional R&D opportunities for AMES. The laboratory director retains the option to identify and support these exceptional types of LDRD projects.

LDRD projects are pursued in forefront areas of basic and applied science and technology that support the DOE mission, enrich Laboratory capabilities, generally advance the knowledge and technology base, and have the potential to generate follow-on funding from DOE offices and programs. Individual LDRD projects will be relatively small and generally fall into one or more of the following categories.

1. Advanced study of hypotheses, concepts, or innovative approaches to scientific, technical, or computational problems.
2. Experiments, theoretical studies, simulations, and analyses directed toward "proof of principle" or early determination of the utility of new scientific ideas, technical concepts and devices, or research tools.
3. Concept creation and preliminary technical analyses of advanced, novel experimental facilities/devices or of facilities for computational science.

LDRD Updates

DOE approved the Ames Laboratory's FY2015 LDRD Plan and expenditures, **not to exceed \$1.3M**. A list of projects begun thus far in FY2015, by project number and title is provided below.

Approved LDRD Plan components:

Novel Projects; Strategic Initiatives; and Exceptional Opportunities (e.g., Spedding Fellow)

Funding Summary (\$ in thousands) for Active Projects

DOE approved the Ames Laboratory's FY2015 LDRD Plan and expenditures. A list of projects active in FY2015 (in \$K), by project number and title is provided below.

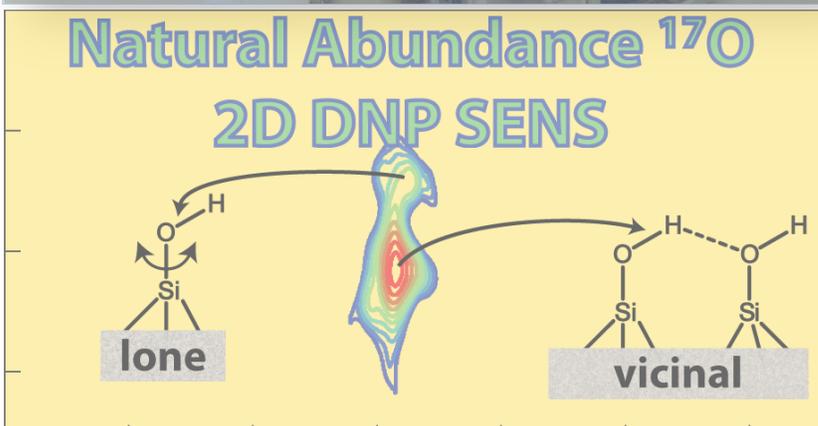
Proposal No.	2013	2014	2015	2016	2017	Total
Novel Projects						
2013-GOR-1218	\$89	\$232	\$169	--	--	\$490
Strategic Initiatives						
2014-LOG-1212	--	\$70	\$72 \$16.4*	--	--	\$142 \$86.4*
2014-SLO-0604	--	\$144	\$118	--	--	\$262
2014-LWA-0413	--	\$55	\$57	--	--	\$112
2014-SAD-0709	--	\$172	\$175	\$180	--	\$527
2015-MPRU-0812	--	--	\$138	\$183	\$190	\$511
2015-VDOB-0909	--	--	\$122	--	--	\$122
2015-JCUI-2008	--	--	\$37.5	\$50	--	\$87.5
2016-MTAN-0815	--	--	\$27	\$145	--	\$172
2016-RPRO-0815	--	--	\$23	\$93	--	\$116
Exceptional Opportunities						
See 2015-MPRU-0812	--	--	\$\$	\$\$	\$\$	0

*Discontinued/Actual

Research Reports



Dynamic Nuclear Polarization NMR



Dynamic Whitelist Generation for Automated Intrusion Response [2013-GOR-1218]

Novel Project: CyberSecurity

PI: Chris Strasburg and Mark Gordon

Project Description

As automation, sophistication, and potential damage of cyber attacks grow the Department of Energy and other organizations are under increasing pressure to automate cyber-defenses, e.g., blocking malicious websites. However, the risk of self-inflicted damage due to such automation is often significant. While resource *whitelists*, i.e., catalogs of resources that should not be disrupted, are one approach to mitigate this risk, manual construction of such lists is inherently error-prone and incomplete. Our goal is to develop an automated, dynamic learning-based approach to identify significant organizational relationships from network flow data, and then also examine its utility. These relationships can then be protected from disruption or identified for additional monitoring by automated cyber-defense mechanisms.

Mission Relevance

Protecting the nation's cyber infrastructure has a broad and direct impact on DOE's mission and also on critical resources, such as the power grid, nuclear stockpile, and the integrity and efficacy of both fundamental and applied research. Improving the automated defense capabilities of organizations at risk of cyber threats has a material impact on mission success throughout DOE.

Results and Accomplishments

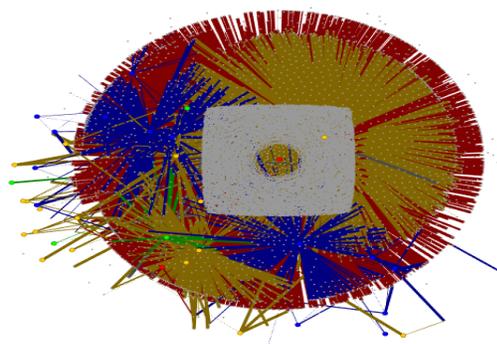
Our initial approach relied on expensive lexical analysis of scarce public web pages related to IP addresses, which does not scale to large or multiple sites, and training data must be labeled. Because models are specific to individual organizations, manually generating sufficient labels is not feasible. Hence, we:

1. Reduced need for website scraping via novel, scalable sources of semantic data for resource characterization;
2. Adapted *social-network-modeling* features to characterize internal and external resources. In particular, we explored the use of bipartite

graph clustering to distinguish between mission-relevant interactions and mission-peripheral activity (Figure 1).

3. Submitted an extended paper to the 2015 Annual Computer Security Applications Conference (ACSAC).

Figure 1 Nodes in the graph's center represent groups of internal hosts, while nodes on the outside represent external resources. The weight on each edge represents the number of days in a month the group has interacted with that particular resource. Edges of different colors represent communication via different services (TCP/IP, SSH, HTTP, SMTP). From this we are working to identify clusters that reveal external resource with maximum impact on an internal group through each service for prolonged time.



Additional Work Product

- Published updated open-source code at: <https://github.com/Ames-Laboratory-Cyber-Group/Cydime>
- Results presented at FloCON 2015, a network-flow based analysis conference.
- Results presented at Super Computing 2015.
- Paper submitted to 2015 Annual Computer Security Applications Conference (ACSAC).
- Initial funding was extended through PNNL for a DOE-wide implementation (work, however, was suspended after one month due to budget constraints).

Proposed Work Next Year

Not Applicable.

Self-Healing, Adaptive Structural Coatings [2014-LOG-1212]

Strategic Initiative: MADD Science (FY14)

PI: Barbara Lograsso

Project Description

A prototype adaptive material is being developed that regulates mechanical properties under service conditions via an artificial structural array of magnetoelastic (ME) phases in a composite to mimic biological mechanoreceptors. ME materials are ferromagnetic materials that change elasticity based on the strength of impinging magnetic fields. Under applied magnetic field and stress, ME phases will resonate at specific property-dependent frequencies. The material is an array of tiny adaptive structures formed by ME and permanent magnet (PM) separated by a flexible substrate. The three-layer structural zones are embedded inside a matrix, and elasticity of the ME materials is altered subject to the PM field strength.

Mission Relevance

Mastering capabilities of living systems to discover, design and synthesize new materials is identified as a BES *Grand Challenge*. We focus on self-adaptive materials that automatically regulate mechanical properties under service conditions, which involve both sensing structure and function, as inspired by organisms that synthesize elaborate structures for multiple functions.

Results and Accomplishments

In response to an applied field impulse, a ME material emits a magnetic flux with a characteristic resonant frequency. Resonant waves are produced, modulated, and detected depending on elasticity, permeability, and magneto-mechanical coupling. The frequency depends upon the magnitude of *dc*-biasing field and mass loading (*pressure or stress*) on the surface. Thus, we measured amplitudes of the longitudinal ME resonant waves versus stress at given magnetic field, and biasing PM phase.

For combinations of ME/Flex/PM trilayers, the scale of microstructure was tested by a minimum distance between ME and PM materials needed for detecting harmonic resonant frequency (*Figure 1*).

Macroscale layer combinations were evaluated to establish candidates for microscale fabrication. Materials (ME & PM) investigated were listed in

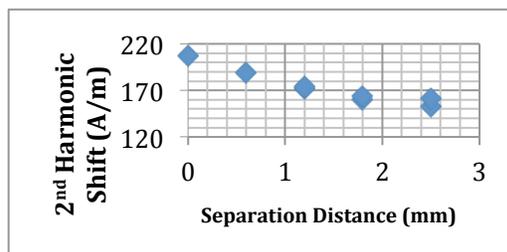


Figure 1 Preliminary resonant harmonic response of the layered materials vs. increasing separation between cast PM material and Metglas 2826.

FY14. Matrix selections represent several orders of magnitude for elastic modulus [2.6 to 200 GPa] to explore range of applicability for these materials, while PM materials showed a range of induction and orders of magnitude of coercivity.

In FY15, fabricating microstructures and examining other candidate materials were started. Testing flexible substrates with varied elasticity to see if useful pressure range can be altered (more rigid substrates increase pressure) were planned.

FY2015 – Project DISCONTINUED

Project was discontinued mid-year FY15 because the PI left Ames Laboratory. No final reportable results were neither accumulated nor published.

Improving Ductility of High-Si Electrical Steel [2015-JCUI-2008]

Strategic Initiative: EdgeS [Late Start]

PI: Jun Cui

Project Description

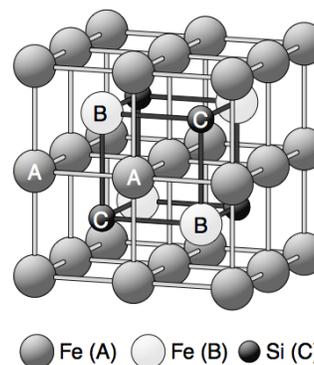
The LDRD project is a short-term effort to validate a materials development strategy to develop a cost-effective manufacturing of high-silicon electrical steel. The effort integrates both computation and experimental exploration with a goal to prove that the A2/B2/DO₃ order-disorder transitions, which are responsible for Fe-Si embrittlement, could be postponed through minor composition modification and processing treatment without sacrificing electric and magnetic properties. An encouraging result could lead to a comprehensive R&D effort on developing new compositions around 6.5% Si enabled by new processing treatments. The anticipated breakthrough for a soft magnetic cost-effective and efficient material could lead to 35% reduction in energy loss from the core, 3% increase in motor efficiency, and more than 228 TWh annual U.S. energy saving.

Mission Relevance

Electrical steel with Fe-3.2%Si is the highest demand soft magnetic material used by motors and power electronics (\$10.2B annual sales in 2014). The material is a compromise of processing cost and performance, which can hinder development of advanced, higher-power density motors and power electronics. The current trend is to increase excitation frequency (especially true for HEVs/EVs traction motors for higher power density (for better \$/kW), but higher frequency results in higher eddy current (higher loss and lower efficiency). For example, a 100 kW motor at 50 Hz with 90% efficiency would deliver 200 kW when running at 100 Hz, but efficiency decreases to 80%. Hence, a ductile, Fe-6.5%Si soft magnet is an opportunity for innovation and dramatic energy savings.

Results and Accomplishments

In this FY15 late-start project, we initiated a study to validate the hypothesis that the A2/B2/DO₃ ordering transitions, responsible for embrittlement, can be postponed through minor composition modification and to show computationally guided materials development is a viable approach for solving the embrittlement problem. Materials have been purchase and initial samples were prepared at year's end. Initial relative phase-stability studies for



α -FeSi Si: 0~5%	A2	All sites are randomly occupied by Fe or Si
α_2 -FeSi Si: 5~5.5%	B2	C, B sites are randomly occupied by Fe or Si
α_1 -FeSi Si: 5.5~10.5%	DO ₃	C sites are randomly occupied by Fe or Si

Figure 1 Crystal structures (occupancy of sublattice sites) for the α (A2), α_1 (DO₃), and α_2 (B2) phases. B2 structure has more slip planes, more ductile. The goal is to validate the possibility to control B2 stability by chemistry and heat treatment.

disordered (A2) and partially ordered (B2 and DO₃) systems were performed using density-functional theory (DFT) based electronic-structure calculations to inform and guide the proposed chemistry, such as ternary or quaternary alloying additions to shift phase boundaries towards higher Si content.

Additional Work Product

Not Applicable.

Proposed Work for Next Year

Hot rolling has been demonstrated to produce thin gauge 6.5% Si steel sheet as the B2 phase is avoided at >700°C; however, higher energy cost and rough surfaces prevents its commercial adoption. Alloying efforts have had limited success, with B, Al, or Cr reported to reduce brittleness but adversely affect coercivity and permeability. There are no published results on quaternary Fe-Si based alloys other than the poor nanocrystalline/amorphous <85% Fe alloy, in which magnetization is diluted by glass-forming elements. Thus, proposed work will focus on alloying guided by theory to avoid embrittled phases, maintain electric and magnetic properties, and keep the manufacturing cost low.

Novel Modular Thermal Conductivity Measurement Setup [2016-MTAN-0815]

Strategic Initiative: EdgeS [Late Start]

PI: Makariy Tanatar

Project Description

We will develop a miniature, modular design of low-temperature thermal conductivity apparatus to enable measurements in variety of cryostats and in precisely aligned, high magnetic fields without dismounting the sample. It will make thermal conductivity measurements **more accessible, extend the available temperature range**, broadening the class of materials studied, and notably **reduce helium consumption**.

This novel, versatile *thermal conductivity module* with mounted samples will be transportable to different magnetic field facilities and enable data collection in the widest range possible without changing the sample mounting or thermometry. This modular device then permits the study of superconducting state of unconventional superconductors, locate the position of nodes on the Fermi surface and address the issue related to possible existence of high-field states.

Mission Relevance

Thermal conductivity measurements in diverse cryogenic and magnetic field environments is a key tool for advanced bulk characterization needed for the initiative involving property measurements, extending ranges of temperature and magnetic field close to operational regimes of high-T_c superconductors.

Results and Accomplishments

Ordered needed materials and supplies to implement design and build of module.

Additional Work Product

Not Applicable, yet.

Proposed Work Next Year

We will complete the build of the thermal module and begin testing. Illustrate how the unit can be switched between three setups for magnetic field, temperature environments, namely, **Kelvinox 400** dilution refrigerator (0.04-2 K range; 0-14 Tesla magnetic field), **PPMS** (1.8-300 K range), and **cryogen-free He3 system** (0.3-300 K range; 0 Tesla). Conduct thermal conductivity measurements on pnictide KFe₂As₂ superconductors without requiring thermometer re-calibration, reducing dramatically experimental time in dilution refrigerator environment and thereby reducing consumption of liquid helium while broadening the available range of temperature in experiment.

Frequency-Domain Magnetic Susceptometer for Pressure and Ultra-Low Temperature [2016-RPRO-0815]

Strategic Initiative: Edges [Late Start]

PI: Ruslan Prozorov

Project Description

The goal is to develop a new technique to measure the high-resolution AC magnetic susceptibility (χ_{ac}) of magnetic and superconducting materials using a tunnel diode resonator (TDR) technique under two extreme conditions: Pressure (~ 20 kbar) and ultra-low temperature (~ 50 mKelvin). This novel P-TDR susceptometer will be extremely useful for studying pressure-induced electronic-structure variation changes to properties of exotic materials, e.g., rare-earth compounds (Ce-Sm-Y)AgSb₂ (itinerant-vs-localized magnetism); frustrated spin-ice (Dy-Tb-Yb)Ti₂O₂; and Fe-based superconductors, like (Ba-K)Fe₂As₂ (strong doping effects). Pressure provides a “clean” parameter to investigate fundamental origins without chemical artifacts. With numerous technical challenges, P-TDR has never been implemented, but we have developed and tested a prototype design for extreme conditions.

Mission Relevance

Measurement of high-resolution AC susceptibility under extreme conditions will reveal fundamental mechanisms responsible for novel magnetic and superconducting materials, and, ultimately, enable the finding of new energy-saving materials. Thus, our research goal is closely aligned to the DOE and Ames Laboratory’s missions. We will make these capabilities available in other Ames Lab’s groups.

Results and Accomplishments

Starting with our tested prototype (Figure 1), we have ordered the needed materials and supplies to implement the build of the proposed design. The change in London penetration depth $\Delta\lambda$ was measured via the P-TDR susceptometer in Figure 1d for pure Pb and shows directly a decrease in superconducting temperature by 1 K for 12 kbar applied pressure compared to 0 kbar. For Ba(Fe-Co)₂As₂ (Figure 1e), $\Delta\lambda$ changed sharply with increased pressure from 12 to 21 kbar, which results from a sharp variation of superconducting gap structure in this range of pressure. Further investigation requires a higher resolution technique.

Additional Work Product

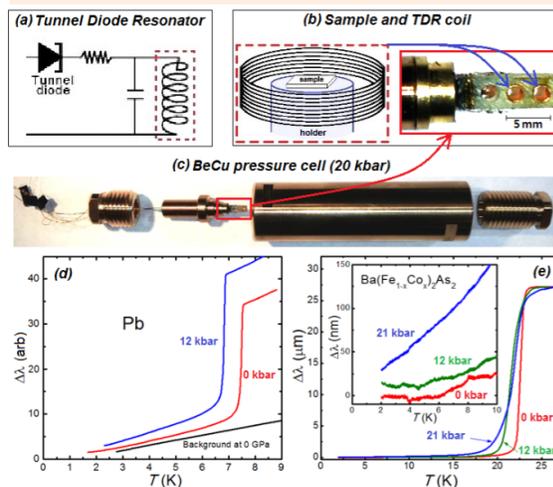
- Not Applicable Yet.

Proposed Work Next Year

- We will complete our susceptometer re-design and build for extreme conditions.

Figure 1 Details of Pressure-TDR (fundamental frequency of 58 MHz) and preliminary data.

(a) Tunnel diode resonator, (b) sample and TDR coil, and (c) piston-cylinder pressure cell (BeCu). Data (d) and (e) are obtained, respectively, from Pb at 0 & 12 kbar, and Ba(Fe_{1-x}Co_x)₂As₂ at 0, 12, & 21 kbar.



Customized Assembly of Catalytic Systems by 3D Printing Technology

[2014-SLO-0802]

Strategic Initiative: GrACE

PI: Igor Slowing and Aaron Sadow

Project Description

This initiative aims to integrate the bottom-up self-assembly of nanostructured materials into mesoscopic arrays with the top-down manufacture of macroscale reactors, to bridge the gap between molecular and macroscopic control of matter. Functionalized catalyst nanoparticle inks will be developed and printed into 3D structures using additive manufacturing technologies. This will enable simple and efficient customization of catalytic setups in the laboratory, and facilitate the translation of fundamental catalyst discovery into process chemistry for industrially relevant conversions. The work aligns with the Ames Laboratory's Strategic Initiative of Greener Advances for Catalysis for Energy (GrACE).

Mission Relevance

DOE-BESAC identified a set of opportunities in mesoscale sciences for clean energy technologies. One of the priority directions is "Directing the assembly of hierarchical functional materials". Combination of this mission with the Grand Challenge in DOE-BESAC's report on Catalysis for Energy: "Design and controlled synthesis of catalytic structures", can be addressed by the merger of novel top-down additive manufacturing technologies with the bottom-up mesoscale self-assembly of nanostructured catalytic materials, which is the target of this project.

Results and Accomplishments

Combination of top-down 3D printing with bottom-up nanostructuring techniques was successfully achieved to produce reactors and active catalysts. A pressure reactor was produced by CAD design and proved capable of working under 5 bar H₂ pressure (Fig. 1a). Several iterations were performed on the reactor design and printing, with significant improvements at each step, proving the relevance of computer-aided design and on site production. The final reactor includes gaskets, ports for pressure gauges, liner, pressure relief valves and catalyst bed with defined geometry incorporated in the path of the reactive gas (Fig. 1a). Novel concept of replaceable catalyst cap inserts (CCI) was coined

and developed into working systems to highlight advantages of computer-aided catalyst production, Fig. 1b. Catalysts for five different reactions were 3D printed and proved to be active (Fig. 1c). Incorporation of nanostructured catalysts into 3D-printed material was demonstrated via electron microscopy and catalytic activity tests (Fig. 1d).

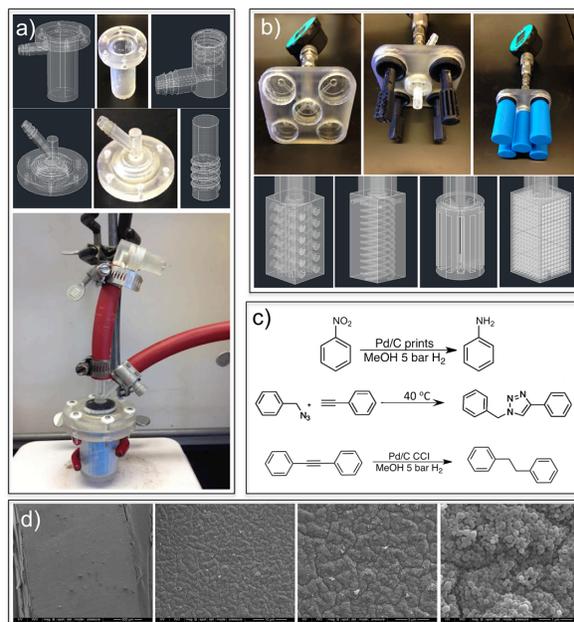


Figure 1. a) 3D-printed pressure reactor containing 3D-printed catalyst. b) 3D-printed, 4-port catalytic reactor for testing catalyst bed configurations, with CAD designs of catalyst cap inserts. c) Catalytic example reactions performed with 3D printed catalysts products. d) SEM images at increasing magnification showing the incorporation of nanostructured mesoporous silica nanoparticle catalyst in a 3D-printed material.

Additional Work Product

- Produced versatile reactor and catalyst platform.
- Demonstrated three catalytic reactions for 3D-printed catalysts.
- **Thesis (M.Sc.)** by J.E. Fleckenstein, "Supported Metal Complexes: From Mesoporous Silica to 3D Printed Polymers," Iowa State University (8/2015).
- **Invited Talk:** "Structural Control of Materials at the Nano-, Meso- and Macroscales by Coupling Additive Manufacturing with Self-Assembly Methodologies," World Materials Research Institutes Forum (9/15/2015), Pleasanton, CA. J.E. Fleckenstein, J.S. Manzano, Z. Weinstein, A.D. Sadow, I.I. Slowing.
- Referred journal manuscripts in preparation.

Adsorption-induced Shape-changing in Nanoalloys: Extended Alloy Wulff Construction with First-principles Calculations [FY2014-LWA-0413]

PI: Linlin Wang

Project Description

We propose to establish the quantitative relation between the shape of nanoalloys (with specific surface composition information) and the coverage of molecule adsorbates for nanoalloys of different sizes and initial bulk compositions, thus to provide designs for heterogeneous (electro)catalysts. This combined continuous and atomistic modeling approach will be developed as part of Thermodynamic Tool Kits (TTK) program to bring the unique capability for nanoalloy design to Ames Laboratory.

Mission Relevance

New findings from *in situ* experimental techniques of nanoalloys at atomic resolution under working conditions demand new computer simulation methods that incorporate the operating environment to explain observations, provide high-throughput predictive capabilities, and design nanoalloys from bottom up. The proposed research will help solve one of the DOE grand challenges to design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties, and help achieve Ames Laboratory's mission.

Results and Accomplishments

The adsorption isotherms were simulated for nanoalloys with adsorbates to determine cyclic voltammetry (CV) during electrocatalysis. The effect of alloying on nanoparticle adsorption isotherms is provided by a *hybrid-ensemble* Monte Carlo (MC) simulation that uses the cluster expansion method extended to non-exchangeable coupled lattices for nanoalloys with adsorbates. Exemplified here for the hydrogen evolution reaction (HER): the 2-dimensional CV is mapped for Pd-Pt nanoalloys as a function of electrochemical potential and global Pt composition, and shows a highly non-linear alloying effect on CV, Fig.1(a). Detailed features in CV arise from the interplay of multi-site H-adsorption that closely correlates to alloy configurations, which are in turn affected by the H coverage. The origins of specific features in CV curves are assigned, Fig. 1(b).

The method provides a more complete means to design nanoalloys for electrocatalytic reactions.

Additional Work Product

- L.-L. Wang, T. L. Tan, & D. D. Johnson, "Nanoalloy electrocatalysis: simulating cyclic voltammetry from configurational thermodynamics with adsorbates", *Phys. Chem. Chem. Phys.*, 17, 28103-28111 (2015).
<http://dx.doi.org/10.1039/C5CP00394F>
- *T. L. Tan, L.-L. Wang, J. Zhang, D. D. Johnson & K. W. Bai "Platinum nanoparticle during electrochemical hydrogen evolution: adsorbate distribution, active reaction species and size effect", *ACS Catalysis* 5, 2376-2383 (2015).
<http://dx.doi.org/10.1021/cs501840c>
- L.-L. Wang, D. D. Johnson & M. C. Tringides "C60-induced Devil's Staircase transformation on a Pb/Si(111) wetting layer", *Physical Review B*, 92, 245405 (2015).
<http://dx.doi.org/10.1103/PhysRevB.92.245405>

*high-impact factor

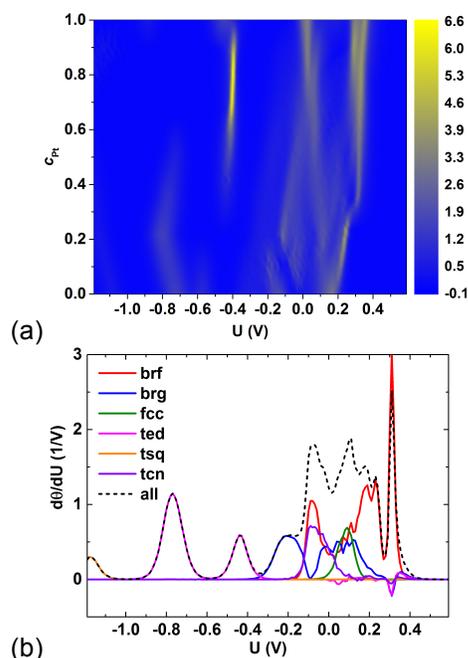


Figure 1 (a) 2D cyclic voltammetry for PdPt alloyed nanoparticles, $d\theta/dU$, a function of both voltage (U) and composition (c_{Pt}). (b) site-decomposed 1D-CV for $Pd_{0.65}Pt_{0.35}$.

Sensitizers for Dynamic Nuclear Polarization (DNP) NMR Spectroscopy

[2014-SAD-0709]

PI: Aaron Sadow, Marek Pruski, Igor Slowing,
William S. Jenks

Project Description

We will prepare and evaluate polarization agents (PAs) for DNP-enhanced solid-state Nuclear Magnetic Resonance (NMR) spectroscopy based on transition-metal compounds and persistent organic diradicals attached to nanometer scale materials. DNP-NMR is an emerging technology that can provide significantly enhanced signals for insight into composition, structure, chemical environment, and bonding in materials. Our goals are to (i) enhance signal sensitivity of DNP-NMR, (ii) provide new radical sensitizers for solvent-free DNP, and (iii) provide support for practical DNP applications to benefit ongoing FWPs. The current PAs are biradicals derived from nitroxyl functionality R₂NO*, e.g., TOTAPOL and bTbK, but their application to a range of materials has not yet developed. From this work, DNP-NMR spectroscopy will allow our researchers to address strategic scientific and technological challenges in energy-related materials.

Mission Relevance

The DOE-BESAC "*Directing Matter and Energy: Five Challenges for Science and the Imagination*" report identifies NMR spectroscopy as a critical tool for catalysts and materials, providing an analytical method to characterize and reveal the control matter and processes for efficient synthesis and energy generation. These sensitization agents are part of an emerging technology central to the DOE's mission to enhance Science and Innovation. Ames Laboratory will lead this effort.

Results and Accomplishments

Our synthesis efforts are directed on solvent-PA and solvent-material interactions. We have prepared and evaluated transition-metal and rare-earth containing paramagnetic centers as DNP PAs following our work with the bTbK backbone. We evaluated surface-attached stable organic radical and di-radical molecule for application in solvent-free DNP. We continue to develop metrics that quantify the relationship between DNP polarization and EPR measurements.

Several key findings make this work extraordinarily beneficial for DNP-NMR applications.

1. We have identified that deuteration of solvents can allow for 2D HETCOR spectroscopy that is not dominated by solvent-derived correlations.
2. We have found that *biradical deuteration* increases enhancement factors in solvents, by up to 70%. (The square of enhancement factors is the improvement to NMR signal-to-noise.)
3. We have also found selective reactivity of polarizing agents with surface species, and this can define the limitations of DNP for analysis of sites.

Additional Work Product

- Perras, F. A.; Reinig, R. R.; Slowing, I. I.; Sadow, A. D.; Pruski, M., Effects of biradical deuteration on the performance of DNP: towards better performing polarizing agents. *Phys. Chem. Chem. Phys.* **2016**, *18*, 65-69. doi: 10.1039/C5CP06505D.

Proposed Work

The work will focus on sample formulation for the application of DNP-NMR to a variety of materials characterization. Controlling the amount of protons available and their location, with respect to radical polarizing agents, greatly affects the enhancement factors. We will be looking to enhance the improvements achieved this year.

Studies of Novel Materials using Dynamic Nuclear Polarization NMR Spectroscopy [FY2015-MPRU-0812]

PI: Marek Pruski

Enhancing DNP-NMR Capabilities – Big GAME-CHANGER for local characterization

Project Description

This LDRD project supports Dr. Frederic Perras' Spedding Post-Doctoral Fellowship to advance the studies of new complex materials using dynamic nuclear polarization (DNP). The project is composed of both a theoretical part, which aims at better understanding the DNP process, as well as an experimental part, which includes the use of DNP-enhanced SSNMR to characterize the structure of new materials in several BES-supported FWPs.

Mission Relevance

DNP SSNMR will provide critical capability for atomic-scale structural elucidations by detecting very small concentrations of NMR-active nuclei, and thereby generate knowledge about several important classes of new energy-related materials, including organic-inorganic hybrids, battery components, and heterogeneous catalysts.

Results and Accomplishments

DNP SSNMR methodology was extended to the ^{17}O nuclide, with the use of the PRESTO sequence, enabling the measurement of undistorted lineshapes, internuclear distances, dynamics, and 2D spectra from surfaces of mesostructured materials. PRESTO was also shown to be generally applicable to quadrupolar nuclei, thus facilitating the characterization of alumina surfaces. We have also demonstrated that, *contrary to conventional wisdom*, DNP is applicable to the study of the surfaces of noble-metal nanoparticles. We have notably applied DNP to determine the structures of low-coverage species that are either bound or have reacted with alumina-supported Pd nanoparticles and used this data to elucidate the breakdown pathway of the catalyst poison: methionine. In a separate study we have also used DNP-enhanced SSNMR in order to characterize dilute, surface-bound, Pd precursors used in the synthesis of monodisperse Pd nanoparticles. Lastly, we have, for the first time, combined ultra-wideline SSNMR with DNP in order to study Pt sites bound to MOF surfaces directly.

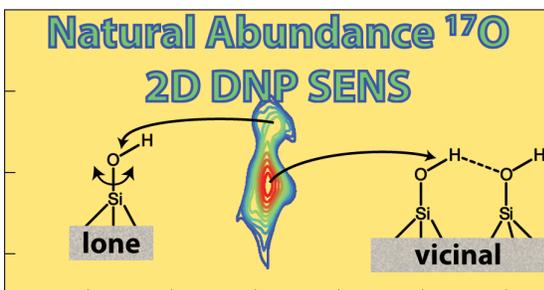


Figure 1 DNP-enhanced, natural abundance $^{17}\text{O}\{^1\text{H}\}$ PRESTO-HETCOR spectrum of MSN surface. Enhanced resolution in the ^1H dimension clearly shows a distinction of lone and vicinal silanols at the surface.

Additional Work Product

- *Perras, F. A.; Kobayashi, T.; Pruski, M. *J. Am. Chem. Soc.* **2015**, *137*, 8336.
DOI: [10.1021/jacs.5b03905](https://doi.org/10.1021/jacs.5b03905)
- Perras, F.A.; Kobayashi, T.; Pruski, M. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22616.
DOI: [10.1039/C5CP04145G](https://doi.org/10.1039/C5CP04145G)
- *Kobayashi, T.; Perras, F.A.; Slowing, I. I.; Sadow, A. D.; Pruski, M., *ACS Catal.* **2015**, *5*, 7055.
DOI: [10.1021/acscatal.5b02039](https://doi.org/10.1021/acscatal.5b02039)
- *Johnson, R. L.; Perras, F. A.; Kobayashi, T.; Schwartz, T. J.; Dumesic, J. A.; Shanks, B. H.; Pruski, M. *Chem. Commun.* **2016**, 52, 1859.
DOI: [10.1039/C5CC06788J](https://doi.org/10.1039/C5CC06788J)
- Perras, F. A.; Chaudhary, U.; Slowing, I. I.; Pruski, M. *J. Phys. Chem. C*, *submitted*.
- *Mouat, A. R.; Whitford, C.; Chen, B.-R.; Perras, F.A.; Pruski, M.; Dedzyk, M.J.; Delferro, M.; Stair, P. C.; Marks, T. J., *J. Am. Chem. Soc.*, *submitted*.
- *Kobayashi, T.; Perras, F. A.; Goh, T. W.; Huang, W.; Pruski, M. *J. Phys. Chem. Lett.*, *submitted*.

*high-impact factor

Proposed Work

In accordance with the goal to better understand the DNP process in an MAS rotor will perform magnetic resonance imaging experiments in order to map how the enhancements are distributed in different sample formulations, and particularly, in the case of ultra-fast MAS. We will also apply DNP to the study of numerous new classes of materials. For example, we will use DNP SSNMR in order to probe correlations between substrates and alumina surfaces in systems that are relevant to the petrochemical industry. We will additionally use DNP in order to probe the formation of paired Sn sites in zeolites. We will also develop DNP as a non-destructive technique to study the structures of biological feedstocks.

Theory and Simulations of Solid-State NMR for Materials Characterization [2015-VDOB-0909]

PI: Viatcheslav Dobrovitski

Project Description

Solid-state nuclear magnetic resonance (SS-NMR) is one of the central characterization techniques for understanding the structure of various complex solid-state materials systems, relevant for DOE mission in energy conversion and storage. Spin diffusion between different kinds of nuclei is a central tool for such studies, as its dynamics sensitively depend on the atomic arrangement. Spin diffusion is also the critical phenomenon driving the *dynamic nuclear polarization* (DNP) enhanced Solid-State NMR: it transfers the high polarization of the electron spins to proton nuclear spins, and then the proton spins to other nuclear spins of interest. We will develop theory and computational tools to investigate the spin dynamics inside large networks of coupled nuclear spins that permit the structural characterization and studies of complex solid-state materials using the. This work will provide new insights and enable interpretation of DNP-NMR signals needed for local environmental characterization of materials.

Mission Relevance

The work will establish a solid theoretical foundation for SS-NMR in complex systems and guide the development of DNP-NMR as a technique to enable Ames Laboratory's DNP studies, ensuring leadership in this area. Results will help guide ongoing and future solid-state DNP-NMR studies of energy-relevant materials, such as catalysts, complex hydrides and correlated-electron materials.

Results and Accomplishments

We developed a set of numerical and analytical approaches for exact and approximate simulations of spin diffusion in SS-NMR. We investigated the method based on a coherent-state representation, potentially allowing modeling of thousands of spins, and created the corresponding computer programs.

With these, we have studied diffusion between different ^{13}C spins in alanine crystals. The method, although approximate, provides good agreement with exact modeling and experiment (Figure 1, upper panels). It now can be used for realistic modeling of many SS-NMR experimental regimes.

Besides accurate description of the spin diffusion, **we predicted a new effect**: ergodicity of the environment of ^{13}C spins (controlled by proton spins) critically affects the ^{13}C - ^{13}C spin diffusion. This finding was qualitatively confirmed in experiments (Figure 1, lower panels).

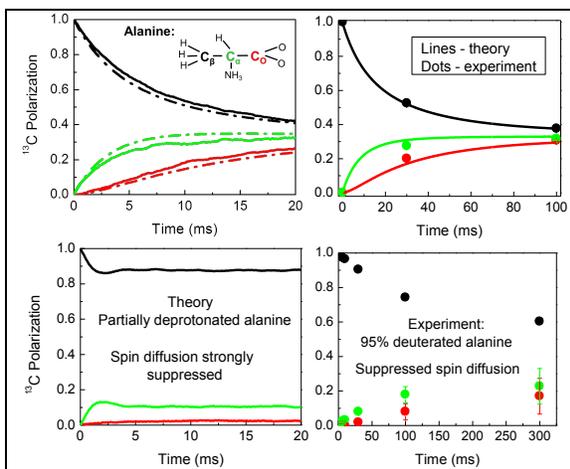


Figure 2 (Upper panels) New model/code accurately reproduces NMR signals of spin diffusion among various ^{13}C spins in alanine crystal. **Left:** Coherent-state (approximate) simulations compared to exact model. **Right:** Predictions compared to experimental data.

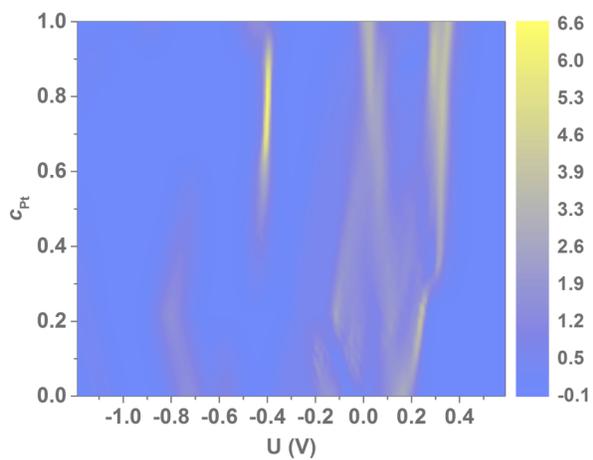
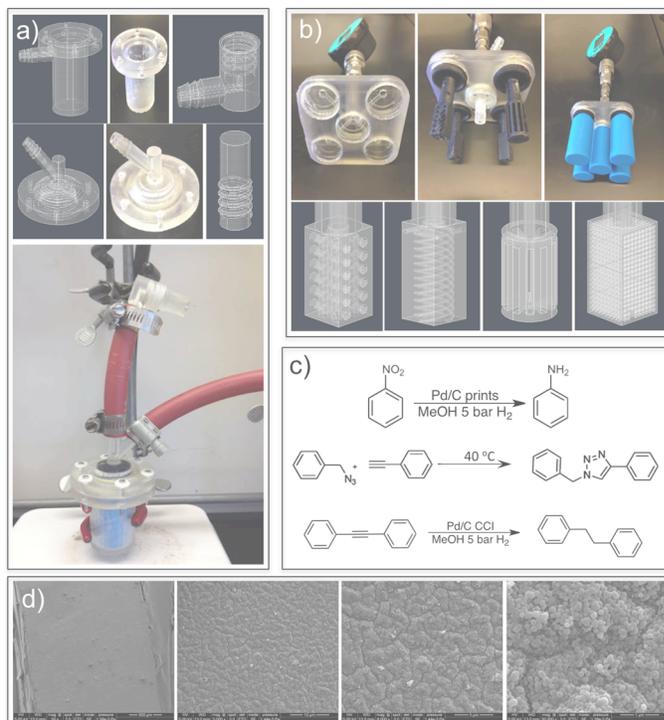
(Lower panels) Left: simulations predict that spin diffusion between different ^{13}C spins in alanine should be strongly suppressed in the absence of ergodicity in the bath of protons, and polarization of different ^{13}C spins do not equilibrate. **Right:** experiments qualitatively confirm the prediction, albeit quantitative differences need to be better understood.

Additional Work Product

- With these significant results, a white paper for proposed FWP on Solid-State NMR Sciences was developed with M. Pruski and A. Rossini, and submitted to DOE/BES/MSED.
- V. Dobrovitski, K. Fritzsche, M. Hong, and K. Schmidt-Rohr, "Modeling of quantum spin dynamics in nuclear magnetic resonance experiments using spin coherent states", *J. Chem. Phys.* (2016), *in preparation*.
- V. Dobrovitski, K. Fritzsche, M. Hong, and K. Schmidt-Rohr, "Impact of non-ergodicity of the proton environment on ^{13}C spin diffusion", *J. Chem. Phys.* (2016), *in preparation*.

Proposed Work Next Year

Not Applicable.



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