MPA MaterialsMatter

February 2009

Credit: Robb Kramer, ADEPS

Sonia Francoual

Heavy fermion explorer

By Tom King
ADEPS Communications

> **Completely changing scientific fields was a perilous and difficult decision.**

The world of Sonia Francoual grew exponentially larger when she was a 14-year-old student in science class. First, she learned how electrons spin around an atom's nucleus like wondrous tiny planets. Then she learned how famed scientist Marie Curie explored the uncharted territory of radioactive elements. These lessons launched Francoual on a lifetime of research on the edge of known quantum physics.

Francoual is a postdoctoral research associate at the National High Magnetic Field Laboratory Pulsed Field Facility (NHMFL-PFF) at Los Alamos National Laboratory. She earned a bachelor's degree in light matter interaction physics and a master's degree in condensed matter physics in France. She focused her early research on the study of quasicrystals using x-ray and neutron scattering techniques.

Francoual said she feels more at home in the laboratory than at huge social events. Nevertheless, in 2004, her thesis advisor Marc De Boissieu pushed her to attend the European Condensed Matter Division Conference in Prague. There, she became enthralled with a completely different conference—one on the physics of 4f and 5f electrons taking place at the same conference center that same week. Francoual said she recalled being so captivated by a presentation by John Singleton of Los Alamos that she began thinking of changing fields entirely. She set her sights on studying the physics of heavy fermions at the Laboratory once she completed her doctoral thesis.

"I met Sonia for the first time during a short visit to Grenoble, France sometime in 2006," said NHMFL-PFF Director Alex Lacerda. "It was clear to me at the time and after talking with my colleagues in Grenoble that

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From Toni's Desk

Susan Seestrom has recently appointed me as one of two MaRIE capability liaisons for the Experimental Physical Sciences Directorate (ADEPS), filling the position that Paul Follansbee vacated last summer. MaRIE, Matter Radiation Interactions in Extremes, is the Laboratory's proposed ~$1 billion signature facility. In this role I will serve as a champion for ADEPS capabilities and needs for MaRIE, as well as a spokesperson for MaRIE to ADEPS, with the goal in both instances of bringing together the broadest suite of people and capabilities to define and promote MaRIE. With this goal in mind, I will use this month's "From the Desk" to describe the MaRIE vision and its role in MPA's strategy. For further information on MaRIE, I encourage you to explore the MaRIE website at marie.lanl.gov.

MaRIE will provide experimental capabilities that will allow Los Alamos to achieve transformational materials performance through predictive multi-scale understanding with an emphasis on radiation-matter interactions. Today, the performance we achieve from many materials is an order of magnitude less than what we believe the fundamental limits to be. This gap reflects our current inability to connect atomic scale phenomena to bulk, integrated performance, i.e., to bridge the "micron gap" from ideal atomic and/or nanoscale materials behavior to real-world materials performance. For example, the strength of a chemical bond has rather little bearing on how strong a given materials component is or how long it will last in the real world. While "bridging the micron gap" overtly refers to a length scale, understanding dynamic and stochastic processes on relevant temporal scales, especially in extreme environments, is central to our vision. To bridge the micron gap, new capabilities are needed to advance, in a transformational way, the frontiers of our understanding of materials performance. MaRIE will achieve this vision.

To accomplish this vision of advancing the frontiers of materials-centric national security science, MaRIE will develop for the first time, and provide to the external scientific community, three unique facilities.

The **Fission and Fusion Materials Facility** will provide unique capabilities for materials irradiation studies, and even more importantly will advance the frontiers of radiation damage science by advancing the field from "cook and look" materials qualification to in situ diagnostics and tailored materials to understand and control radiation damage.

The **Multi-Probe Diagnostic Hall** will provide unprecedented probes of matter including (for the first time) simultaneous measurements of materials interactions at relevant temporal, spatial, and spectral resolutions. These tools will advance the frontiers of dynamic materials performance spanning from solidification phenomena to turbulence in warm dense matter in which a solid is no longer a solid.

The **M4 (Making, Measuring, and Modeling Materials) Facility** will discover by design the next generation of materials to perform with orders of magnitude better durability in these extreme environments. M4 will also discover and translate to utilization the next generation of integrated solid state solutions for renewable energy and detection. Translating new quantum and nanoscale discoveries so that they can be used for practical applications requires the same capability to bridge the micron gap from atomic scale understanding to device performance that is required to understand and exploit the limits of materials strength.

All three facilities are essential to fulfill this vision. MaRIE will be the first capability with unique co-located tools necessary to realize transformational advances in materials performance in extremes.

The success of MaRIE is important for the future of MPA Division, just as leadership and engagement from MPA in defining MaRIE are essential for the success of MaRIE. MPA has, and will continue to play, a central role in defining, developing, and promoting MaRIE. Eighteen months ago John Sarrao left his position as MPA's first Division Leader to lead the conceptual design and acquisition strategy as MaRIE Capture Manager. Mark McClesky of MPA-MC leads the planning process for the M4 facility, while others in MPA participate in planning for the Multi-Probe Diagnostic Hall and the Fission and Fusion Materials Facility. The credibility of MaRIE as a materials-centric national user facility is based on the Laboratory's successes in the operation of the Center for Integrated Nanotechnologies, the National High Magnetic Field Laboratory, and Lujan Center. The M4 facility is modeled after CINT (albeit on a much

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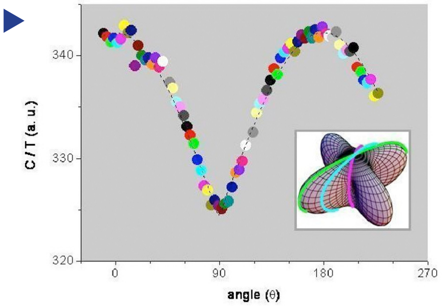
Martinez receives Presidential Early Career Award for Scientists and Engineers

Jennifer Martinez

Jennifer S. Martinez (MPA-CINT) received a prestigious Presidential Early Career (PECASE) Award for Scientists and Engineers. John Marburger, science advisor to President George W. Bush and director of the White House Office of Science and Technology Policy, presented the award to Martinez at the White House. She is one of 67 researchers to receive the award, which is the highest honor the U.S. government bestows to outstanding scientists early in their careers. Nine federal departments and agencies annually nominate scientists and engineers whose work shows exceptional promise for leadership at the frontiers of scientific knowledge for the PECASE Award. The Award embodies the high priority the government places on maintaining the leadership position of the U.S. in science by producing outstanding scientists and engineers who will broadly advance science and the missions important to the participating agencies. Each PECASE recipient receives up to five years of research funding from the nominating agency. Martinez is one of eight Department of Energy (DOE)-funded researchers to be recognized.

In addition to her work using biomolecular recognition strategies to template, solubilize, and assemble nanomaterials, Martinez is active in development of biosensors that could have applications in medical diagnostics and in detection of biological threat agents. Her research has been published in *Science*, *Proceedings of the National Academy of Sciences, Journal of the American Chemical Society*, and *Langmuir*. She collaborates with visiting researchers and collaborators at the Center for Integrated Nanotechnologies, one of several DOE national user facilities focused on nanotechnology research. She received a Los Alamos award for mentoring postdoctoral scientists. The DOE Office of Science, Office of Basic Energy Sciences, funded her achievements cited in the PECASE Award.

Probing nodal superconductivity



Modulation of specific heat with magnetic field direction for $CeRhIn_5$ at a pressure of 1.4 GPa. Depending on the position of nodes, where the superconducting gap function goes to zero, Doppler effects on superconducting Cooper pairs lead to a modulation in the specific heat as a function of field angle along particular crystallographic directions. Inset: Examples of polar field sweeps that pass through the poles and equatorial plane of a superconducting gap with s+g symmetry.

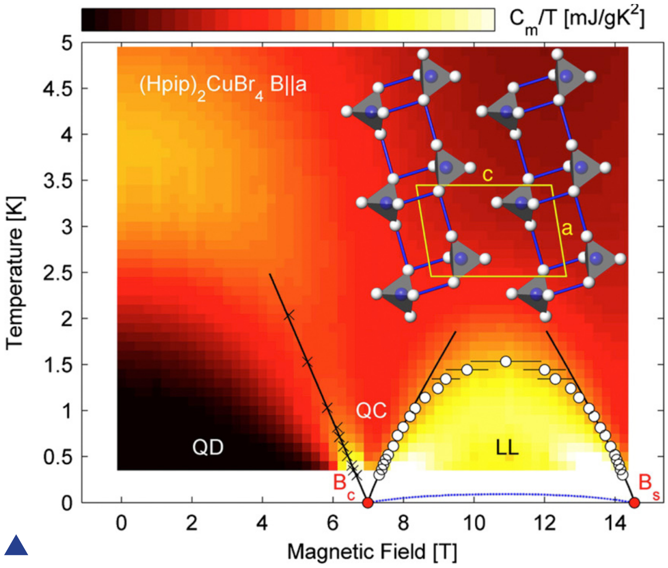
The emergence of superconductivity near an antiferromagnetic quantum critical point suggests that magnetic fluctuations associated with the quantum critical point may provide a glue to form electron pairs. In these unconventional superconductors, the superconducting order parameter, which is tied closely to the superconducting pairing mechanism, breaks the underlying crystalline symmetry and contains nodes at which the superconducting gap becomes zero on the Fermi surface. The presence of nodal quasiparticles qualitatively changes the density of states at the Fermi level and leads to a powerlaw temperature dependence of thermodynamic properties. This power-law behavior contrasts with the exponential temperature dependence in fully gapped conventional superconductors and, therefore, provides an indicator of unconventional superconductivity.

In heavy-fermion superconductors, where the relationship between superconductivity and quantum criticality is most conspicuous, experimental data of the superconducting gap are rarely available because of disorder from chemical substitution or pressure environments that are needed to induce superconductivity. Tuson Park, Eric D. Bauer, and Joe D. Thompson (all in MPA-10) conducted high pressure, field-rotation specific heat measurements to probe the nodal gap structure as the heavyfermion superconductor, $CeRhIn_5$, is tuned toward its magnetic quantum-critical point. This is the first example where such studies have been possible and the first determination of the momentum-dependent superconducting order parameter in any pressure-induced superconductor. The measured momentum dependence of the superconducting gap is inconsistent with the theoretically predicted p-wave, spin-singlet gap. However, the measured dependence is consistent with a d-wave superconducting gap with line nodes. This result constrains a theory of interplay between superconductivity and antiferromagnetism and provides insight into the pairing mechanism in strongly correlated superconductors. Reference: “Probing the Nodal Gap in the Pressure-Induced Heavy Fermion Superconductor $CeRhIn_5$”, *Physical Review Letters* **101**, 177002 (2008). Los Alamos research was performed under the auspices of the Department of Energy Office of Science and supported by the Laboratory Directed Research and Development program.

Spin Luttinger liquid behavior confirmed in an organic quantum magnet

When magnetic systems are constrained to one dimension, long-range magnetic order cannot occur due to phase fluctuations. Instead, a Luttinger liquid phase is predicted to form in which the magnetic excitations become delocalized, and the correlations between spins decay algebraically rather than exponentially. Quantum magnets that are truly one dimension in nature are extremely rare. A new organic quantum magnet, piperdinium copper bromide [(HPIP) $_2$-CuBr$_4$], is a prototypical two-leg ladder material. This material is the first example in which one-dimensional behavior dominates over a significant region of temperature and magnetic field. Therefore precise comparisons between experiment and theory can be made to test the hypothesis of a spin Luttinger liquid. All phases of interest (quantum disordered, quantum critical, and spin Luttinger liquid) can be accessed.

Vivien Zapf (MPA-NHMFL) and collaborators at the University College London, the Helmholtz Center Berlin, the Paul Scherrer Institute in Switzerland, the Ecole Polytechnique Federale de Lausanne, the University of Geneva, CNRS (National Center for Scientific Research) in Toulouse, the University of Toulouse, and the University of Bern examined the phases of (HPIP) $_2$-CuBr$_4$. The scientists combined extensive theoretical modeling with neutron scattering, specific heat and magnetization to confirm that Luttinger Liquid behavior extends over a region of phase space between 2K and 70 mK, and between 7 and 15 T. The findings show that the crossover into the Spin Luttinger Liquid is demonstrated by clear features in both the specific heat and magnetization of the material. Reference: “Thermodynamics of the Spin Luttinger Liquid in a Model Ladder Material,” *Physical Review Letters* **101**, 247202 (2008).



Field-temperature phase diagram of the spin–ladder compound [(HPIP) $_2$-CuBr$_4$, showing quantum disordered (QD), quantum critical (QC), and spin Luttinger-liquid (LL) phases. The contour plot shows the magnetic specific heat as $C_m(T,B)/T$. Local maxima from the reduction of the tripletgap by the Zeeman effect are indicated by crosses. Circles denote the LL crossover based on measurements of the magnetocaloric effect, black lines are fits to extract the critical fields, and the dashed blue line indicates the onset of long-ranged order below 100 mK. Inset: lattice structure of [(HPIP) $_2$-CuBr$_4$in projection along the b axis, with copper (Cu) atoms blue and bromine (Br) white.

Desk. .

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larger and more comprehensive scale), both in terms of the user facility model and the emphasis on spanning materials capabilities from synthesis, characterization, and modeling to integration. Finally, MaRIE enables the Laboratory’s materials strategy, a key component in the future of MPA Division, ensuring our engagement in key national directions of material science, as well as providing resources to enable strategic investment for the materials strategy.

The current vision for MaRIE is a result of broad-based and critical participation of our technical staff. I encourage MPA staff to engage in this vital effort. Right now MaRIE is in the early stages of pre-conceptual design, with the MaRIE team defining the functional requirements for MaRIE based on a combination of sponsor and community needs, science roadmaps, and an integrated analysis of competing facilities. In particular, to ensure the validity and credibility of the vision, Los Alamos is engaging the external technical community through a series of workshops in 2009 in articulating the scientific drivers and facility requirements for MaRIE. Many MPA staff recently participated in a MaRIE workshop on “Research Frontiers and Capability Gaps for Controlling and Designing Functional Materials,” the purpose of which was to identify and define capability gaps mainly relevant to the M4 facility. This community engagement will culminate in December with an externally-led workshop on “Decadal Challenges for Predicting and Controlling Materials Performance in Extremes,” resulting in a community-driven report defining decadal scientific challenges and capability gaps.

Finally, although MaRIE is an essential part of the future of both MPA and the broader materials capability at Los Alamos, it is realistically 10 years in the future. Our near-term and long-term strategies cannot be totally consumed by MaRIE or we will fail before we get there. Yet, we must include MaRIE science and capabilities as an important component in our strategic planning process for the materials capability for MPA and the Laboratory.

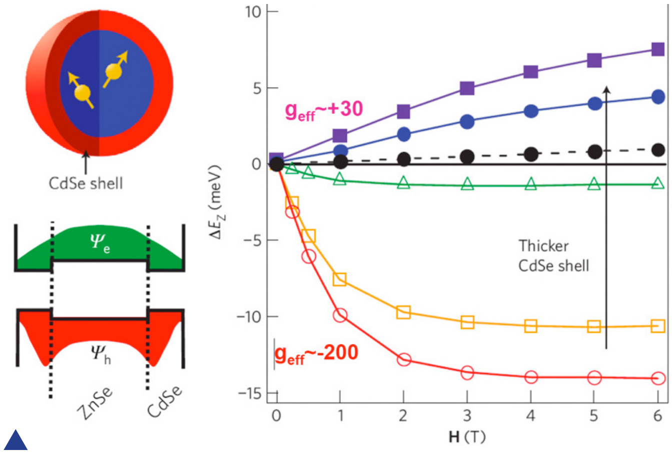
— MPA Division Leader Toni Taylor

Tunable semiconductor nanocrystal quantum dots

Two papers, one in *Nature Materials* and one in *Physical Review Letters*, describe the interplay between high magnetic fields and spin-polarized electrons (and holes) in specially designed semiconductor nanocrystal quantum dots. These works come from a collaboration in MPA-CINT, MPA-NHMFL, and C-PCS.

The *Nature Materials* paper describes a tunable magnetic exchange interaction between electron-hole excitations in a nanocrystal and magnetic manganese ions (Mn^{2+}) that are incorporated into the nanocrystal. Magnetic doping of semiconductor nanostructures is pursued for applications in magnetic memory and spin-based electronics. These applications require control of the interaction strength between carriers (electrons and holes) and the embedded magnetic atoms. Colloidal nanocrystal structures provide great flexibility through growth-controlled "engineering" of electron and hole wavefunctions in individual nanocrystals. Researchers developed semiconductor quantum dots with a widely tunable magnetic exchange interaction between electron-hole excitations (excitons) and magnetic manganese ions in the nanocrystal. The materials are "inverted" core/shell nanocrystals composed of zinc selenide (ZnSe) cores and manganese ions, covered with nonmagnetic shells of narrower-gap cadmium selenide (CdSe). Low-temperature optical studies of magnetic circular dichroism reveal giant Zeeman spin-splittings between the spin ±1 band-edge excitons that are tunable both in magnitude and in sign. The CdSe shell thickness tunes effective exciton g-factors. This research demonstrates that growth-controlled engineering of nanocrystal structures is a feasible route to tunability. Reference: D. Bussian, S. Crooker, M. Yin, M. Brynda, A. Efros and V. Klimov, *Nature Materials* **8**, 35 (2008).

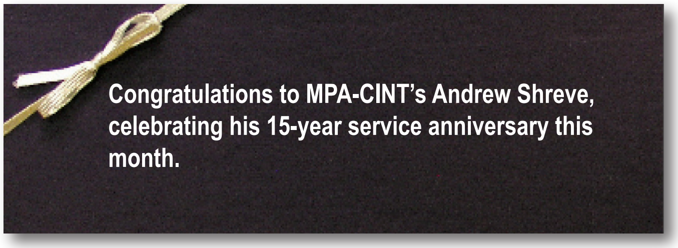
The *Physical Review Letters* paper describes optical photoluminescence studies of single semiconductor nanocrystal quantum dots in a high magnetic field. The nanocrystals are composed of non-magnetic CdSe. In typical ensembles of nanocrystals, optical emission and absorption resonances are significantly broadened by the inhomogeneous (5-10%) size distribution of the particles. This broadening has confounded attempts to quantify the small spin-splittings and Zeeman-energy shifts that are induced by magnetic fields. However, the low-temperature photoluminescence linewidth of an individual nanocrystal is quite narrow. The narrow photoluminescence lines observed from single nanocrystals at low temperature make it possible to spectrally resolve, for the first time, a clear Zeeman splitting between right- and left-circularly polarized photoluminescence (which arises from the recombination of spin-up and spin-down exciton states). The data reveal exciton g-factors at the single-quantum-dot level, and also show an anomalous polarization behavior in nanocrystals possessing an internal shape asymmetry. Reference: H. Htoon, S. Crooker, M. Furis, S. Jeong, A. Efros and V. Klimov, *Physical Review Letters* **102**, 017402 (2009).



Schematic of Mn-doped ZnSe nanocrystal cores (17 A radius), overcoated with a CdSe shell, which ranges from 0-8 A in thickness. Band diagrams show notional electron and hole wavefunctions in the nanocrystal. The plot shows measured Zeeman splitting of the band-edge exciton as a function of magnetic field. The effective exciton g-factor varies from -200 to +30, depending on shell thickness.

Affiliations: D. Bussian, H. Htoon, S. Jeong, and V. Klimov (C-PCS, MPA-CINT); S. Crooker (MPANHMFL); M. Yin and M. Brynda (UC, Davis); M. Furis (U. Vermont); and A. Efros (Naval Research Lab). The LDRD program, the DOE Office of Science, Chemical Sciences, Biosciences, and Geosciences Division; and the DOE Center for Integrated Technologies (CINT) supported the work.

Celebrating service



Congratulations to MPA-CINT's Andrew Shreve, celebrating his 15-year service anniversary this month.

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Francoual . .

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she was a very hard working young researcher. I'm pleased I was able to attract Sonia to a postdoctoral tenure here with us."

Completely changing scientific fields was a perilous and difficult decision. "In Europe it would be considered wasting education" to make such a leap, she said. She wrote researchers at Los Alamos with a proposal to study heavy fermions. Their response was enthusiastic.

The first half of 2006 was a whirlwind for Francoual. She finished writing her thesis at the end of February and wrote her Los Alamos proposal four days later. In April, she successfully defended her thesis and in May received an offer letter from Los Alamos. Thrilled, she said she announced to her parents, "I'm going to America!"

Moving to New Mexico—sight unseen—was a bold move for Francoual. "You have to have a dream to drive you forward," she said, but she didn't hesitate, because "I was sure I would love it here."

At Los Alamos, she helped develop the dilatometry technique for measurements in very high magnetic fields and at very low temperatures. Her ultimate goal was to probe magneto-elastic effects in magnetic and electronic systems such as heavy fermions, quantum magnets, and multiferroics.

Today, she studies the effects of rhenium doping and emergent ferromagnetism on the itinerant electron metamagnetism in URu2Si2. She measures magnetoresistance and magnetization in pulsed magnetic fields at low temperatures. She also studies magneto-elastic effects in URu_2Si_2 doped with 4% rhodium. She measures thermal expansion and magnetostriction in DC fields up to 45 T between 1.5 K and 30 K. Mentor Neil Harrison (MPA-NHMFL) said, "Sonia gets very involved in complicated things."

Exploring the unknown territory of heavy fermions and quasicrystals has not satisfied Francoual's scientific curiosity. Next, she hopes to study the mysterious properties of quadrupolar ordering and spin density wave systems. "If the project I am working on is fascinating, it keeps me motivated, no matter how challenging or difficult it might be," she said.

Francoual is still inspired by the pioneering spirit and intellectual enthusiasm of Marie Curie, who was the first female professor at the University of Paris, the first person to win two Nobel Prizes, and the discoverer of the elements radium and polonium. "You can make a difference in science when your heart is in it," she said.

"She is indeed very hard working and she accomplished and learned a lot in a field of research very different to the one she was used to," Lacerda said. "Soon Sonia will be moving back to Europe and she will be starting a job in Hamburg, Germany."

Striving for scientific accomplishment has always come easy to Francoual, but there is one bit of interpersonal communication she has so far been unable to accomplish. Her life was forever changed when she heard a Laboratory scientist speak in Prague, and she now works at that same Laboratory—in the same group. But she has never gathered up the courage to tell him how his presentation changed her life.

"The Laboratory allows me to immerse myself in science and forget who I am," she said. "To be here is like fulfilling a dream."

Bose-Einstein condensation in a quantum magnet measured to new low temperature

Vivien Zapf (MPA-NHMFL) and collaborators at the High B/T (magnetic field/temperature) Laboratory at the University of Florida-Gainesville and the Universidade de Sao Paulo have confirmed Bose condensation in an organic quantum magnet using magnetization measurements down to a 1 mK.

This is the first time this phenomenon has been measured in a quantum magnet down to such low temperatures. The lower-temperature data provide more accurate and robust comparisons between experiment and theory than had been obtained previously. The scientists studied an organic quantum magnet $NiCl_2$-$4SC(NH_2)_2$, in which the nickel magnetic moments form a Bose condensate in magnetic fields between 2 and 12 tesla. Studying condensation of bosons in quantum magnets provides important information about this fundamental state of quantum matter in the thermodynamic limit of large numbers of particles.

Reference: "Direct Measurement of the Bose-Einstein Condensation Universality Class in $NiCl_2$-$4SC(NH_2)_2$ at Ultralow Temperatures," *Physical Review Letters* **101**, 187205 (2008).

The National Science Foundation, the DOE, and the State of Florida through the National High Magnetic Field Laboratory funded the work.