

Annual Scientific Report for Grant No. DE-FG03-03NA00067

Title of the Grant "Development of Designer Diamond Technology for High-Pressure-High Temperature Experiments in Support of the Stockpile Stewardship Program"

Principal Investigator: Yogesh K. Vohra, University of Alabama at Birmingham (UAB)
Support Period: 01/12/03 to 11/30/2004

Research Progress:

Simultaneous Electrical and Structural Measurements on Neodymium Metal to 152 GPa

Using designer diamond anvils and angle dispersive x-ray diffraction technique at a synchrotron source we have performed simultaneous electrical and structural studies on Neodymium metal to 152 GPa in a diamond anvil cell. In the pressure range between 100 to 152 GPa, four-probe electrical resistance measurement shows a 38% decrease in the electrical resistance associated with the delocalization of the 4f-shell electrons. The continuous decrease in electrical resistance is consistent with the observation of a gradual phase transition to α -U structure in this pressure range. The (111) diffraction peak of α -U structure first appears at 100 GPa and increases in intensity with increasing pressure to 152 GPa. This increase in intensity is attributed to an increase in structural y-parameter from 0.07 at 118 GPa to 0.95 at 152 GPa. Unlike Cerium and Praseodymium, continuous evolution of α -U structure and electrical resistance in Neodymium confirms the gradual nature of 4-f delocalization process.

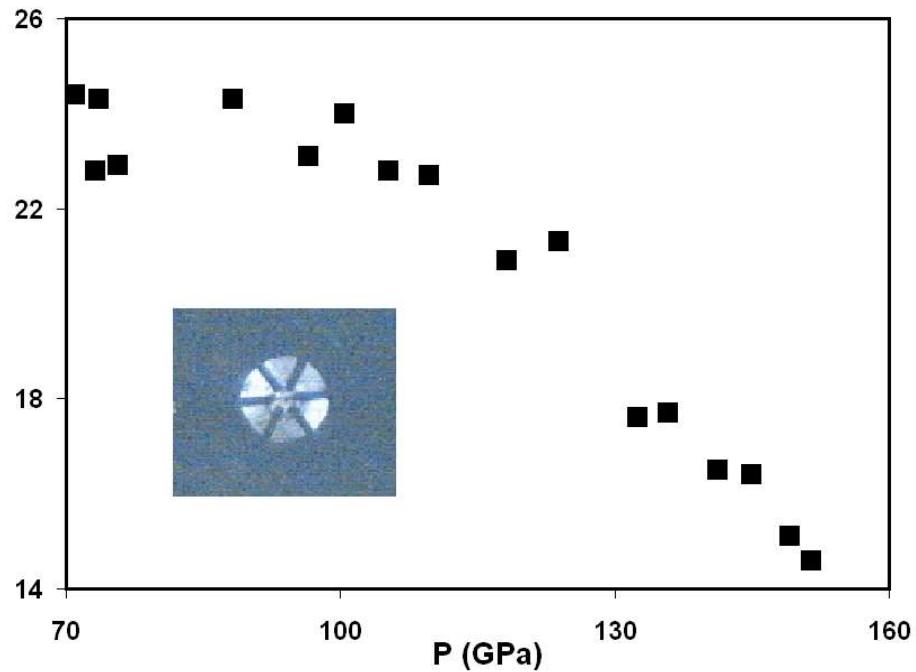


Figure 1: Change in electrical conductivity in Nd metal with increasing pressure. At lower pressure, the four-probe electrical resistance measurements show an average value of 23.1 mΩ. As the pressure is increased above 100 GPa we observe a steady decrease of 38% to 14.6 mΩ at 152 GPa. The insert shows an optical micrograph of the designer diamond anvil with Nd sample in the gasket hole of a spring steel gasket. The central flat, as shown, is 100 μ m in diameter and the sample chamber is \sim 50 μ m. Simultaneous structural measurements were carried out at the HPCAT synchrotron facility at the Advanced Photon Source, Argonne National Laboratory.

From Fig. 1 we see that the electrical resistance measurements on Nd in the pressure range from 71 GPa to 100 GPa show a steady average value of about 23.1 mΩ. As pressure is increased and the α -U phase continues to develop, the electrical resistance starts to decrease. This decrease is consistent with having more electrons in the conduction band due to *f* electrons becoming itinerant. The decrease in the resistance value is not sudden, but yet continues to decrease steadily from 23.1 mΩ at 100 GPa to 14.6 mΩ at 152 GPa. This is also consistent with what is observed from the x-ray spectra. After indexing the spectra at 118 GPa to the α -U phase we are able to continue assigning all the spectra to this phase up to the highest pressure of 152 GPa. The gradual drop in electrical resistance correlates well with the variation in positional *y*-parameter of the alpha-Uranium structure in Neodymium.

Ohmic Heating Studies Using Designer Diamond Anvils

Using an eight-probe designer diamond anvil, ohmic heating was demonstrated for the first time on a tungsten sample up to 50 GPa and temperature of 2900 K. The pressure was measured by the ruby fluorescence technique and the sample temperature was characterized by the black body emission. Machining a pit in the designer diamond and filling it with alumina powder achieved the thermal insulation of sample. This technology has a great promise in generating high pressure-high temperature data on *f*-electron systems critical to the stockpile stewardship program.

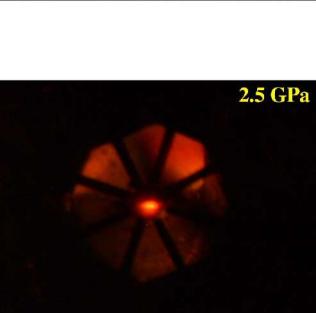
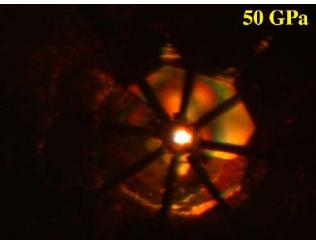
In this reporting period, we have demonstrated successful heating of high-pressure samples in a diamond anvil cell (Fig. 2). Eight electrical probes are used to send current and heat the high-pressure tungsten specimen at 50 GPa to 2900 K as measured by the black body emission from the hot sample. These ohmic heating designer anvils will be employed in high-pressure high temperature studies on heavy rare earth metals.

Joule Heating Using Designer Diamonds

Figure 2: Demonstration of heating a high-pressure tungsten sample. The left panel shows a tungsten sample at 50 GPa and 2900 K. The right panel shows the same tungsten sample at 2.5 GPa and at a lower temperature of 1200 K.

Isotopically-Enriched Designer-Diamond Anvils

We have studied optical defect centers and surfaces of isotopically enriched diamonds grown on diamond anvils by microwave plasma CVD. We have used isotopically enriched designer diamond anvils in high-pressure diamond anvil cells to study the effect of isotopes on diamond properties. Isotopes were used to grow homoepitaxial diamonds with *labeled* isotopes of carbon and nitrogen. The isotopic enrichment of carbon and nitrogen was 0.01, 0.41, 0.83, and 0.99 as determined from Raman spectroscopic measurements. The diamonds were grown between 80K and 320K using micro-photoluminescence excitation with a krypton laser excitation source. The defect spectra of the diamonds were taken from nitrogen-related defect centers at nominal energy of 1.77 eV (575 nm defect), especially for the non-(100) surfaces. The defect spectra show ZPL's at 1.77 eV and 1.68 eV are observed, but the 1.77 eV ZPL appears to be associated from the original diamonds, while the 1.68 eV ZPL is known to originate with silicon-based defects. Atomic Force Microscopy of as-grown isotopically enriched layers show rough growth steps in areas with surface roughness of hundred nanometers and smooth areas with surface roughness of few nanometers. Our studies indicate that (100) polished surfaces of isotopically enriched designer diamonds with low concentration of nitrogen defect centers can be



amond anvil. Upper panel shows tungsten sample at

opically enriched layers for applications as various mixtures of methane isotopes of 0.01, 0.41, 0.83, and 0.99 studied at temperatures up to 320 K with an argon ion and zero phonon lines (ZPL) at 1.77 eV (575 nm defect) and 2.156 eV (630 nm defect) faces fluoresced weakly. The 1.77 eV ZPL appears to be associated from the original diamonds, while the 1.68 eV ZPL is known to originate with silicon-based defects. Atomic Force Microscopy of as-grown isotopically enriched layers show rough growth steps in areas with surface roughness of hundred nanometers and smooth areas with surface roughness of few nanometers. Our studies indicate that (100) polished surfaces of isotopically enriched designer diamonds with low concentration of nitrogen defect centers can be

fabricated for a variety of applications in high pressure research. Figure 3 shows summary of Raman spectra of all the isotopically enriched diamond grown in this study.

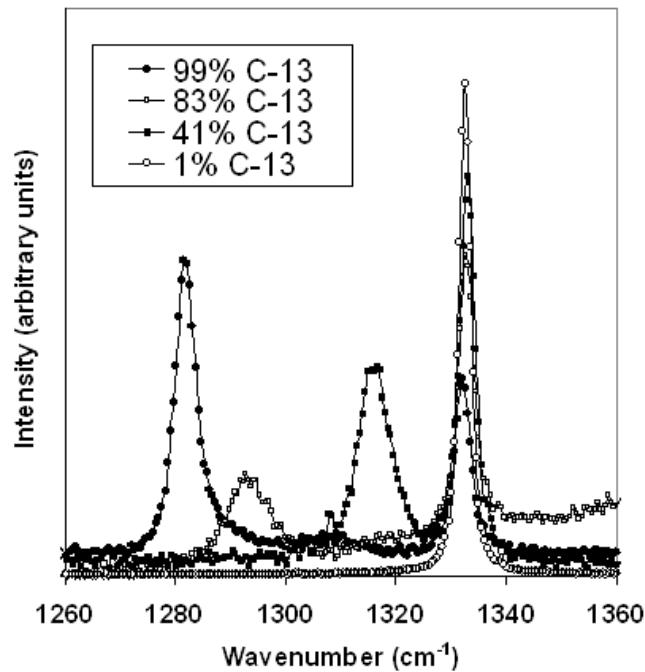


Figure 3: Micro-Raman spectra of three isotopically enriched diamonds and one natural abundance diamond (1% C-13) showing Raman peak from the grown isotopically enriched layer and the underlying substrate. Laser excitation wavelength is 514.5 nm. The substrate Raman peak is always at 1332 cm⁻¹ while the isotopically enriched layer Raman peak position depends on the ¹³C concentration.

Theoretical Modeling of Light Actinide Metals at High Pressures

We have carried out full potential linear muffin tin orbital calculations of total energies for Thorium (Th), Protactinium (Pa), and Uranium (U) under high pressures to explain the observed structural trends and measured compressibility of these light actinides. The face-centered cubic to body centered tetragonal transformation in Thorium at 63 GPa was reproduced in the theoretical model and served as a benchmark to validate the computer code. The full potential linear muffin tin orbital calculations on Pa and U are currently in progress.

Support of Graduate Students

Two graduate students Kevin Hope and Douglas White are currently supported by this grant. Kevin Hope has implemented a Full Potential Linear Muffin Tin Orbital electronic structure code at UAB for calculations of the high-pressure structural transformations in rare earth and actinide metal metals.

• Collaboration with Lawrence Livermore National Laboratory (LLNL)

All research papers listed below have been written in collaborations with scientists at LLNL. Graduate student Kevin Hope has visited Lawrence Livermore National Laboratory and carried out collaborative work in theoretical modeling of behavior of light actinide metals at high pressure.

Research papers accepted or submitted for publication in peer reviewed journals (Included in the Appendix):

- (1) Randolph S. Peterson, Paul A. Baker, Shane A. Catledge, Yogesh K. Vohra, Samuel T. Weir, “Optical Defect Centers and Surface Morphology of Isotopically Enriched Diamond Layers in Designer Diamond Anvils”, Journal of Applied Physics **97**, 073504 (2005).
- (2) Nenad Velisavljevic, Yogesh K. Vohra, and Samuel T. Weir, “Simultaneous Electrical and X-ray Diffraction Studies on Neodymium Metal to Ultra High Pressures” to be submitted to High Pressure Research (2005).

Stewardship Science Academic Alliances Program Symposium, March 29-31, 2004, Albuquerque, New Mexico: PI Yogesh Vohra made a presentation at this SSAA symposium and graduate students Kevin Hope and Doug White presented their work in form of poster presentations.

Personnel Supported:

Name	Percentage Effort
PI Yogesh Vohra	8 %
Dr. Shane Catledge	50 %
Kevin Hope (Graduate Student)	100 %
Doug White (Graduate Student)	100 %

Grant is on track financially for this year.