Progress 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”

Principal Investigator: Yogesh K. Vohra, University of Alabama at Birmingham (UAB)

Support Period: 01/12/02 to 11/30/2003

Research Progress:

- Standardization of fabrication procedure for the designer diamond anvils

In the Year 1 of this project, we have achieved 100 % success rate in the fabrication of designer diamond anvils. This was achieved by reducing the nitrogen contamination in the processing chamber, replacement of a oil based vacuum pump by a dry scroll pump, and reducing the line widths of the side pads in the lithographic fabrication of the electrical probes. The lithographic fabrication of the electrical probes was carried out at the Lawrence Livermore National Laboratory. The problems of crack formation near the metal probes during polishing on the side of the designer diamonds were completely eliminated in this optimized process. This is a major step forward in the development of designer diamond technology.

- Isotopically Enriched Designer Diamond Anvils

Isotopically enriched designer-diamond anvils were grown by microwave plasma chemical deposition using methane/hydrogen/oxygen chemistry. These isotopically enriched diamond layers can modify the thermal properties of the culet of high-pressure anvils and also allow the use of $^{13}\text{C}/^{12}\text{C}$ Raman pressure sensor system for high-pressure high-temperature measurements. Raman spectroscopy clearly revealed the isotopically mixed nature of the culet while the photoluminescence spectra at 80 K demonstrates the nitrogen-based defect center near the culet of the diamond anvil. The ability to isotopically modify the diamond culets offers yet another functionality for the embedded electric and magnetic sensors in a designer-diamond anvil. We have studied nitrogen-related defects in the photoluminescent spectra from diamond films grown homoepitaxially on diamond anvils by chemical vapor deposition with isotopically enriched methane. Various mixtures of methane isotopes were used to grow homoepitaxial diamond with ^{13}C molar fractions of 0.01, 0.43, 0.84, and 1.0 determined from Raman shifts of the usual 1332.5 cm^{-1} line. Defect centers were studied at temperatures between 80K and 320K using micro-photoluminescence spectroscopy. The 514.5 nm line from an argon-ion laser was used for excitation at powers between 100 mW and 800 mW. The defect spectra were dominated by zero phonon lines (ZPL) from nitrogen-related centers at nominal energies of 1.945 eV and 2.156 eV, especially for the non-(100) surfaces. Polished (100) surfaces fluoresced weakly. The ZPL energies and the phonon side-band energy splittings change with isotopic composition, as do the Raman lines. ZPL's at 1.77 eV and 1.68 eV are observed, but not for all isotopic samples. The 1.77 eV ZPL appears to be associated with the original diamonds, while the 1.68 eV ZPL is known to originate with silicon-based defects.

- Crystallographic Anisotropy in Compression of Uranium Metal to 100 GPa

X-ray diffraction studies were carried out on Uranium metal (99.9 %) in a diamond anvil cell to 100 GPa (Volume compression $V/V_0 = 0.700$) at room temperature using a variety of pressure markers like ruby, copper, and platinum. The diffraction patterns are carefully indexed allowing for reversal of peak positions based on anisotropic compression. We report anisotropic compression of the orthorhombic unit cell with the axial ratio b/a increasing initially to 40 GPa followed by a rapid decrease at higher pressure. On the other hand, axial ratio (c/a) shows a rapid increase with increasing pressure followed by saturation at megabar pressures. The most recent

full potential electronic structure calculations reproduce the increasing trend of axial ratio c/a to 100 GPa but do not explain the variation in the b/a ratio. Our detailed analysis of all available experimental data also indicates that the observed anisotropic effects are intrinsic to Uranium and are independent of the pressure medium used in the high-pressure experiments.

- Electrical Studies on Praseodymium Metal Using designer Diamond Anvils

The electrical and magnetic properties of light rare earth metals and trans-plutonium actinide metals are of interest to probe the behavior of f-shell delocalization under high compressions. Using designer diamond anvil technology, sensitive electrical four probe measurements were performed on light rare earth metal Praseodymium to pressures of 56 GPa at room temperature. We document a resistivity drop of 48 % at a pressure of 20 GPa. This large drop in resistivity provides the strongest experimental evidence yet for the view that the 20 GPa phase transition is indeed associated with f-electron delocalization. Our results show that the precise electrical measurements are ideally suited for f-delocalization studies, especially, where structural data do not provide clear evidence of this transition.

- Support of Graduate Students

Two graduate students Kevin Hope and Douglas White are currently supported by this grant and they plan to finish their thesis work by 2005 under this project. Kevin Hope is implementing 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. Douglas White is involved in the electrical measurements with designer diamond anvils at UAB.

- Collaboration with Lawrence Livermore National Laboratory (LLNL)

All three-research papers listed below have been written in collaborations with scientists at LLNL. PI has made two research trips to LLNL this year to work on collaborative projects.

Research papers accepted or submitted for publication in peer reviewed journals (papers included as an appendix to this progress report):

1. Paul A. Baker, Yogesh K. Vohra, Randolph S. Peterson, and Samuel T. Weir, "Isotopically Enriched Designer-Diamond Anvil", Applied Physics Letters, Volume **83**, Number 9, 1 September 2003.
2. Yogesh K. Vohra, J. Reed Patterson, and Jagannadham Akella, "Crystallographic Anisotropy in Compression of Uranium Metal to 100 GPa", resubmitted to Physical review B, August 16th, 2003.
3. Kirkland M. MacMinn, Nenad Velisavljevic, Yogesh K. Vohra, and Samuel T. Weir, "Electrical Measurements of f-Electron Delocalization in Praseodymium Metal at High Pressures Using Designer Diamond Anvils", Submitted to Physical Review Letters, August 5th, 2003.

Research papers to be presented at the national meetings:

1. Yogesh K. Vohra, J. Reed Patterson, and Jagannadham Akella, "Crystallographic Anisotropy in Compression of Uranium Metal to 100 GPa", abstract submitted for the Fall Materials Research Society Meeting in Boston, MA, December 1-5, 2003.
2. Yogesh K. Vohra, Randolph S. Peterson, Paul A. Baker, and Samuel T. Weir, "Defect Centers in Isotopically Enriched Chemical Vapor Deposited Designer Diamond Anvils", abstract submitted for the Fall Materials Research Society Meeting in Boston, MA, December 1-5, 2003.
3. Qi Liang, Shane Catledge, and Yogesh K. Vohra, "Mechanical Properties of Boron Doped Diamond Film Prepared by MPCVD", abstract submitted for the Fall Materials Research Society Meeting in Boston, MA, December 1-5, 2003.

APPENDIX

(Copies of the three research papers acknowledging support from Grant No. DE-FG03-03NA00067)

Isotopically-Enriched Designer-Diamond Anvil

(paper # 1)

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Isotopically-enriched (42 at. % ^{13}C) designer-diamond anvils were grown by microwave plasma chemical deposition using methane/hydrogen/oxygen chemistry. These isotopically-enriched diamond layers can modify the thermal properties of the culet of high-pressure anvils and also allow the use of $^{13}\text{C}/^{12}\text{C}$ Raman pressure sensor system for high-pressure high-temperature measurements. Raman spectroscopy clearly revealed the isotopically mixed nature of the culet while the photoluminescence spectra at 80 K demonstrates the nitrogen-based defect center near the culet of the diamond anvil. The ability to isotopically modify the diamond culets offers yet another functionality for the embedded electric and magnetic sensors in a designer-diamond anvil.

PACS: 62.50.+p, 78.55.-m, 81.15.Gh

Diamond anvils are brilliant cut diamonds used in high-pressure experiments in a diamond anvil cell (DAC). Designer diamond anvils are diamond anvils to which sensors can be incorporated and are encapsulated with chemical vapor deposited diamond whose physical properties can be modified¹⁻². For high-pressure experiments at high temperature, such as electrical heating with micro-coils in a DAC, it is desirable to reduce the thermal conductivity of diamond to thermally insulate the culet from the bulk of the anvil. It is well known that isotopic mixing of diamond can lower the thermal conductivity of diamond³. Isotopically pure diamond has a thermal conductivity that is 50% higher than that of natural abundance diamond crystals⁴. It is also desirable for pressure-sensing applications to have a pure ¹³C diamond culet so that a ¹²C diamond chip can be used in a sample chamber as a pressure-temperature sensor in a high-pressure, high temperature diamond anvil cell⁵. Therefore, there is a motivation to produce designer diamond anvils where diamond culets can be modified by isotopic mixing of ¹²C and ¹³C for electrical heating of samples in a DAC as well as for pressure sensing applications. This letter reports on the synthesis and characterization of isotopically enriched diamond layers on top of a 0.3-carat brilliant cut diamond anvil that is typically utilized in high-pressure research.

Figure 1 shows a fully fabricated designer diamond anvil containing two vertically integrated sensors, including an eight-probe circuit for electrical measurements and electrical heating and a micro-loop for magnetic susceptibility measurements². These sensors were placed at various depths in the diamond anvil with the eight-probe pattern on top and the micro-loop pattern underneath. The diamond deposition was carried out in two stages to encapsulate the two different sensors. However, to fully utilize the capability of electrical heating elements in a designer diamond anvil, the thermal conductivity of the culet must be decreased to thermally insulate the heating elements from the bulk of diamond and from other sensors placed in the diamond. The present experiments are geared towards achieving this goal during the homoepitaxial growth of diamond by using a microwave plasma chemical vapor deposition process.

Figure 2 (a) shows a culet of a typical 0.3-carat brilliant cut diamond anvil used in high-pressure research. This diamond anvil is of natural abundance and contains 98.9 at. % ¹²C and 1.1 at. % ¹³C and is cut with [100] direction perpendicular to the culet face. Homoepitaxial

diamond deposition was carried out using isotopically enriched methane in a hydrogen-oxygen plasma using microwave plasma chemical vapor deposition. The diamond substrate temperature was maintained at 1212 ± 1 °C during the two hour deposition period. The plasma was maintained with a gas flow rate of 500 sccm of hydrogen, 5 sccm of $^{12}\text{CH}_4$, 5 sccm of $^{13}\text{CH}_4$, and 1 sccm of oxygen. The chamber pressure in the plasma reactor was 90 Torr, and the microwave power was 1100 Watts. Figure 2 (b) shows the as grown crystal at the same magnification as Figure 2 (a). Figure 2 (c) is a close-up of the isotopically- enriched diamond culet showing the diamond growth steps indicating high-quality growth and the absence of diamond twins and inclusions⁴. The orientation of the growth steps with respect to cubic directions in the plane of the culet is also indicated in Figure 2 (c).

Confirmation of the isotopic enrichment of the diamond culet and a quantitative determination of the ^{13}C content of the deposited film was obtained with micro-Raman spectroscopy. Figure 3 shows the Raman spectrum of the isotopically enriched diamond layer recorded using the 514.5 nm green excitation of an Argon ion laser. The spectrum from the substrate shows a single Raman peak at 1332.5 cm^{-1} while a doublet containing two peaks at 1315.5 cm^{-1} and 1332.5 cm^{-1} is observed from the isotopically enriched layer. It should be also noted that Raman peak due to the isotopically mixed layer at 1315.5 cm^{-1} (FWHM of 8.8 cm^{-1}) is broader than the peak due to the substrate (FWHM of 5.0 cm^{-1}) and is attributed to the effects of isotopic disorder⁶. The intensity ratio of these peaks is a function of the thickness of the isotopically enriched layer and is a function of the geometry of the culet. The observed Raman frequency of the isotopically mixed diamond layer can be used for a quantitative determination of the ^{13}C content in our film. The following relationship between the frequency and the composition as given by D'Evelyn et al⁷ was used in the quantitative determination of ^{13}C content of the film:

$$\nu (\text{cm}^{-1}) = 1332.96 - 37.52 x - 5.63 x^2 - 8.35 x^3,$$

where x is the molar fraction of ^{13}C in the film. Using the measured frequency from Figure 3 of 1315.5 cm^{-1} , we find that the ^{13}C isotopic content of the film is 42 at. %.

It is also important for the high-pressure applications of these diamonds that the optical fluorescence properties are investigated and various optical defect centers be documented. We have recorded the low temperature photoluminescence (PL) spectra from a variety of positions on the isotopically enriched homoepitaxial diamond layer. The optical properties of the diamond culet are of particular importance in the spectroscopic applications of the DAC. Figure 4 shows the PL spectrum from the substrate and the isotopically enriched layer at a low temperature of 80 K excited by 514.5 nm line of an Argon ion laser. The PL spectrum from the initial substrate shows a low fluorescence background with only one Zero Phonon Line (ZPL) at 1.77 eV. This defect center is often observed in natural diamond. There is an increase in the diamond fluorescence after homoepitaxial diamond growth due to incorporation of nitrogen-related defect centers characteristic of chemical vapor deposition. In particular, sharp emission lines or Zero Phonon Lines (ZPL) are observed at energies of 1.945 eV and 2.16 eV. These are attributed to the Nitrogen-Vacancy (N-V) pair and Nitrogen-Interstitial (N-I) pair respectively and these ZPL's are accompanied by broad phonon side bands to the lower energy sides. The strong red fluorescence from the enriched diamond masks the 1.77 eV system from the original substrate. We also observe that there is a non-uniform distribution of these nitrogen related defect centers and their concentration is larger in the non- (100) facets of the homoepitaxial diamond.

In summary, we have shown that an isotopically enriched, homoepitaxial diamond layer can be grown on brilliant cut diamond anvils. These isotopically enriched layers can be used to lower the thermal conductivity of diamond near the culet for fabrication of electrical heaters in designer diamond anvils. In addition, fabrication of a designer diamond anvil with a pure ^{13}C tip will allow the use of a ^{12}C diamond chip as a pressure-temperature sensor. The capability to modify the thermal conductivity and the Raman spectrum of the culet adds new functionality for the embedded sensors in a designer diamond anvil, and will allow for the use of diamond as a pressure sensor under extreme pressure-temperature environments.

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FIGURE CAPTIONS:

Figure 1: Optical micrograph of a culet of a fully fabricated designer diamond anvil containing multiple microcircuits including an eight-probe pattern for electrical measurements and electrical heating and a micro-loop pattern for magnetic susceptibility measurements. These microcircuits are encapsulated in a chemical vapor deposited layer and are at different depths in the anvil with eight-probe pattern above and micro-loop pattern underneath.

Figure 2: Homoepitaxial deposition of an isotopically mixed diamond layer on a diamond anvil. (a) Starting substrate of natural isotopic abundance, (b) Isotopically enriched layer after two hours of deposition on (a), and (c) high resolution image of the surface showing growth steps on the surface. The [010] and [001] cubic directions are indicated in the plane with [100] direction perpendicular to culet face.

Figure 3: The comparison of the Raman spectra recorded from the isotopically mixed diamond layer and of the substrate. The isotopically mixed layer shows a clear doublet as compared to the single peak observed from the substrate.

Figure 4: The comparison of the fluorescence spectra recorded from the substrate (lower curve) and the isotopically mixed diamond layer (upper curve) at a low temperature of 80 K. The isotopically mixed layer shows additional characteristic nitrogen based defect centers incorporated during chemical vapor deposition.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

**Crystallographic Anisotropy in Compression of Uranium Metal to 100 GPa
(paper # 2)**

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X-ray diffraction studies were carried out on Uranium metal (99.9 %) in a diamond anvil cell to 100 GPa (Volume compression $V/V_0 = 0.700$) at room temperature using a variety of pressure markers like ruby, copper, and platinum. The diffraction patterns are carefully indexed allowing for reversal of peak positions based on anisotropic compression. We report anisotropic compression of the orthorhombic unit cell with the axial ratio b/a increasing initially to 40 GPa followed by a rapid decrease at higher pressure. On the other hand, axial ratio (c/a) shows a rapid increase with increasing pressure followed by saturation at megabar pressures. The most recent full potential electronic structure calculations reproduce the increasing trend of axial ratio c/a to 100 GPa but do not explain the variation in the b/a ratio. Our detailed analysis of all available experimental data also indicates that the observed anisotropic effects are intrinsic to Uranium and are independent of the pressure medium used in the high-pressure experiments.

PACS: 62.50.+p, 61.50.Ks, 81.30.Bx

The light actinide metals (Th-Pu) have always occupied unique placement in the periodic table because of their itinerant 5-f electrons and complex crystallographic phases at high pressures and high temperatures.¹ The contributions of 5-f electrons to bonding gives rise to low symmetry crystal structures and a narrow 5f-band pinned to the Fermi-level. The high-pressure studies on 5-f metals have always played a key role in modifying their electronic structure due to band broadening and electron transfer effects among various electronic sub-bands under high pressures. In particular, Uranium metal has been a subject of intense theoretical and experimental investigations²⁻⁵ and published data to 100 GPa and 4500 K has established the existence of orthorhombic (α -phase), body centered tetragonal (β -phase), and body centered cubic (γ -phase). At room temperature, orthorhombic α -phase is known to be stable to 100 GPa. In a most recent study on Uranium metal to 100 GPa with silicon and nitrogen pressure media⁶, a revised value of the bulk modulus of Uranium of 104 GPa was obtained. However, changes in axial ratio with pressure and anisotropic compression effects have not been discussed in detail even though changes in diffraction line shapes are readily observable in x-ray studies below 100 GPa. This study is motivated by the anisotropic compression of a, b, and c-axis in the orthorhombic Uranium and a careful x-ray diffraction analysis has been performed using a variety of pressure markers. We also correlate these anisotropic compression effects in Uranium to the changes in electronic structure induced by compression. It is also interesting to point out that anisotropic thermal expansion effects are well documented in the α -Uranium phase at low temperatures.⁷ It is known that the b-axis of the α -Uranium phase has the lowest thermal expansion coefficient as compared to a-axis and c-axis in the temperature range of 78 to 298 K.

The polycrystalline samples of Uranium metal were studied in a diamond anvil cell to 100 GPa at room temperature. The goal of this study was to investigate the anisotropy in compression of alpha-Uranium phase at ultra high pressures and obtain a precise equation of state using a variety of pressure standards. In particular, we were interested in the anisotropic compression of the a, b, and c-axis of the orthorhombic unit cell of Uranium and its effects on the ordering of various (hkl) diffraction peaks observed in the diffraction patterns to pressures of 100 GPa.

Three separate high-pressure experiments were performed on Uranium metal in a diamond anvil cell. Two high-pressure experiments were performed at The University of Alabama at Birmingham (UAB) and a third experiment was performed at the Lawrence Livermore National Laboratory (LLNL). We did not use any pressure-transmitting medium in these experiments as our primary pressure range of interest lies above the freezing pressure of most pressure transmitting mediums. The UAB experiments used commercially available Uranium foil of 99.98 % purity (20 x 25 mm, thickness of 0.178 mm). In the first experiment at UAB, we utilized ruby as a pressure sensor, and the energy dispersive x-ray diffraction data was collected to pressure of 41 GPa. In the second experiment at UAB, copper was used as a pressure standard, and x-ray diffraction data was collected to 100 GPa. The third experiment at LLNL used a high purity Uranium sample with platinum as a pressure standard and x-ray diffraction data was collected to 100 GPa. All x-ray diffraction patterns were collected at the beam line X-17C at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory with a micro-collimated beam of 10 microns x 10 microns. The ruby calibration⁸, copper equation of state⁹, and platinum equation of state¹⁰ were employed in our pressure measurements on Uranium sample.

The α -Uranium phase is orthorhombic with four atoms at $(0,y,1/4)$, $(0,-y,3/4)$, $(1/2,1/2+y,1/4)$, and $(1/2,1/2-y,3/4)$ with internal positional parameter $y = 0.105$ at ambient conditions. In our experiments, we have not determined the y -positional parameter from the measured x-ray intensities, as we are primarily interested in the unit cell dimensions from the observed diffraction line positions. In an earlier study⁶, it was shown that the y -parameter is insensitive to pressure up to at least 100 GPa. The ordering of diffraction peaks in the α -Uranium phase is strongly dependent on the axial ratios like c/a and b/a as explained below. The Uranium diffraction pattern at low-pressure shows characteristic triplet diffraction peaks consisting of (110), and (021), and (002) Bragg planes. At ambient pressure, (002) diffraction peak appears to the right of (110) and (021) diffraction peaks of the orthorhombic phase. As pressure increases, this triplet set of peaks merge in to a single diffraction peak because of the anisotropy in the compression of three axes of the unit cell. The least compressibility of the c -axis implies that the (002) diffraction peak does not increase in energy as rapidly as the (110) and (021) diffraction peaks with increasing pressure. This results in a single merged diffraction

peak by 25 GPa in Uranium sample. As the pressure is increased beyond 50 GPa, the diffraction peaks separate out again with (002) now appearing on the left side of the (110) and (021) diffraction peaks. Figure 1 shows this peak reversal at 100 GPa, where (002) diffraction peak now appears on the left side of (110) and (021) diffraction peaks of the orthorhombic phase. In Figure 1, uranium diffraction peaks are indexed to an orthorhombic phase and the copper pressure standard is indexed as an FCC phase.

Figure 2 shows the variation of the axial ratio (b/a) as a function of pressure for the data obtained in all three experiments. The b/a ratio increases initially with increasing pressure till 40 GPa, after that a rapid decrease is observed which continues till the highest pressure of 100 GPa. The measured b/a ratio between ambient and 100 GPa can be fitted to a fourth order polynomial as shown below.

$$b/a = 2.055 + 8.765E-04 P - 6.322E-07 P^2 - 2.582E-07 P^3 + 1.680E-09 P^4$$

The pressure P is measured in GPa and the b/a fit is valid from $0 \leq P \leq 100$ GPa.

On the other hand, axial ratio (c/a) in Figure 3 shows a rapid increase with increasing pressure during initial compression. This increase in c/a ratio continues till a pressure of 60 GPa and there is a tendency of c/a ratio to saturate above this pressure. The measured c/a axial ratio was fitted to the following third order polynomial in the pressure range from ambient to 100 GPa.

$$c/a = 1.732 + 2.071E-03 P - 1.563E-05 P^2 + 4.029E-08 P^3$$

The pressure P is measured in GPa and the c/a fit is valid from $0 \leq P \leq 100$ GPa.

It can be argued that the observed crystallographic anisotropic compression effects are some how related to the non-hydrostatic compression conditions experienced by the Uranium sample in a diamond anvil cell. However, comparison of our experimental data with that obtained with liquid nitrogen or silicone oil medium⁶ show virtually similar axial ratio variations

with pressure. Therefore we believe that the observed anisotropic compression effects are intrinsic to Uranium sample and are independent of any non-hydrostatic compression in a diamond anvil cell.

Figure 4 shows the composite equation of state of Uranium metal to 100 GPa at room temperature using data obtained with ruby, copper, and platinum pressure markers. The measured volume compression of Uranium at 100 GPa, V/V_0 is 0.700. It is remarkable that the measured equation of state with three different pressure markers gives very consistent results.

Birch-Murnaghan EoS of third-order¹¹, Eq. 1, was fitted for pressure range 0.1 MPa to 100 GPa.

$$P = 3B_0 f_E (1 + 2f_E)^{5/2} \left[1 + \frac{3}{2}(B' - 4)f_E \right] \quad (1)$$

Where B_0 is the bulk modulus, B' is the first derivative of bulk modulus, B'' is an implied value of the second derivative of bulk modulus, given by:

$$B'' = \frac{-1}{B_0} \left[(3 - B')(4 - B') + \frac{35}{9} \right]$$

and $f_E = \frac{\left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]}{2}$, for volume at room temperature-pressure, V_0 . Using Eq. 1 following values were obtained:

$$V_0 = 82.94 \text{ \AA}^3$$

$$B_0 = 128.4 \text{ GPa}$$

$$B' = 4.451$$

$$B'' = -0.0354 \text{ GPa}^{-1}$$

Our equation of state parameters are in general agreement with previously published data on Uranium to 100 GPa²⁻⁵.

The electrostatic energy in the α -Uranium structure is known to favor an orthorhombic arrangement with an axial ratio $c/a = 1.82$, $b/a = 1.98$, and positional parameter $y = 0.140$. These optimal values are based on a simple model⁴ where electrostatic energy is expressed as simple monopole sum and resulting minima in electrostatic energy corresponds to the above-mentioned parameters. It should be added that this simple electrostatic model is independent of atomic number Z or crystal potentials and only depends on the variation of Madelung constant due to distortion of the orthorhombic unit cell. Our experimental data on c/a shows a rapid increase from ambient value of 1.737 to a value of 1.826 at 100 GPa (Figure 2) consistent with the minimum in the electrostatic energy. However, variation in the b/a ratio is not in agreement with the prediction of the simple electrostatic model. The electrostatic model would predict the b/a ratio to decrease from ambient pressure value of 2.057 to 1.98 with increasing pressure. Instead, our experimental measurements indicate that b/a first increases from ambient value of 2.057 to 2.077 at 41 GPa before showing a rapid decrease at higher pressure reaching a value of 2.045 at 100 GPa. The b/a value at 100 GPa is still higher than 1.98 value predicted by the simple electrostatic model. Recently, Full Potential Linear Muffin Tin Orbital (FPLMTO) electronic structure calculations⁶ have been carried out to 100 GPa, these calculations reproduce the increase in c/a ratio with pressure rather well. However, a monotonous decrease in b/a with increasing pressure is predicted by the electronic structure calculations in contrast to the experimental data. The c -axis of the orthorhombic cell is the least compressible in the entire pressure range to 100 GPa with a measured compression $\Delta c/c$ of 8.2% at 100 GPa. The a -axis is observed to be more compressible than the b -axis in the pressure range between ambient pressures to 83 GPa. There is a crossover point at 83 GPa, above which the b -axis is observed to be the most compressible. This trend is in agreement with the most recent FPLMTO electronic structure calculations⁶, however, the crossover point is calculated to be at a lower pressure near 30 GPa.

In summary, we have measured the crystallographic anisotropy effects in the compression of the orthorhombic phase of Uranium metal. We observe very interesting variation in both axial ratio (b/a) and (c/a) with increasing pressure to 100 GPa. Our results indicate that the c -axis in the orthorhombic cell is the least compressible in the entire pressure range to 100 GPa and there is a crossover point in the compression of a -axis and b -axis of the orthorhombic

cell at 83 GPa. The most recent FPLMTO calculations reproduce the increasing trend of axial ratio c/a to 100 GPa but do not explain a maximum in the (b/a) ratio. Our detailed analysis of all available experimental data also indicates that the observed axial ratio trends are independent of pressure media used or non-hydrostatic stresses on the sample. The measured static equation of state of Uranium is presented to 100 GPa and a good level of consistency is obtained with three different pressure markers in the diamond anvil cell experiments.

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FIGURE CAPTIONS:

Figure 1: Energy dispersive x-ray diffraction pattern at a pressure of 100 GPa from Uranium sample and a copper pressure marker in a diamond anvil cell. The copper (Cu) diffraction peaks are indexed due to an FCC phase and Uranium (U) peaks are indexed according to an orthorhombic phase. The diffraction angle $\theta = 6.494$ degrees.

Figure 2: The pressure variation of the axial ratio (b/a) for three different experiments employing ruby, copper, and platinum pressure markers. The b/a ratio shows a maximum at approximately 40 GPa. The solid curve is a polynomial (Poly.) fit described in the text.

Figure 3: The pressure variation of the axial ratio (c/a) for three different experiments employing ruby, copper, and platinum pressure markers. The c/a ratio shows an initial rapid increase with pressure and then saturates above 60 GPa. The solid curve is a polynomial (Poly.) fit described in the text.

Figure 4: The measured equation of state of Uranium to 100 GPa at 300 K. The data is a composite of three different pressure markers as noted. The solid curve is a fit to The Birch-Murnaghan equation of state (EoS Fit) described in the text.

Figure 1

Figure 2

Figure 3

Figure 4

Electrical measurements of f-electron delocalization in praseodymium metal at high pressures using designer diamond anvils

(paper # 3)

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Abstract

The electrical and magnetic properties of light rare earth metals and trans-plutonium actinide metals are of interest to probe the behavior of f-shell delocalization under high compressions. Using designer diamond anvil technology, sensitive electrical four probe measurements were performed on light rare earth metal Praseodymium to pressures of 56 GPa at room temperature. We document a resistivity drop of 48 % at a pressure of 20 GPa. This large drop in resistivity provides the strongest experimental evidence yet for the view that the 20 GPa phase transition is indeed associated with f-electron delocalization. Our results show that the precise electrical measurements are ideally suited for f-delocalization studies, especially, where structural data do not provide clear evidence of this transition.

The divalent and trivalent rare earth metals at ambient pressure have a localized 4-f shell and trans-plutonium actinide metals have a localized 5-f shell at ambient conditions giving rise to remarkably similar physical properties. The application of external pressure is expected to cause delocalization of these bound electrons and dramatically modify the electronic, magnetic, and thermal properties as well as equation of state of these metals. In the past several decades, the f-shell delocalization phenomenon in light rare earth metals and trans-plutonium actinide metals under high pressures has always motivated condensed matter theorists and experimentalists to refine computational methods and improve high pressure techniques.¹⁻⁴ This transition from a localized f-shell to an itinerant f-band is usually accompanied by a large volume collapse (10 to 20 %) in light rare earth metals like Cerium at 0.7 GPa. This volume collapse is also accompanied by appearance of low symmetry crystal structures characteristic of f-bonding like the orthorhombic alpha-Uranium structure. In fact, in both Cerium and Praseodymium, alpha-Uranium phase is known to exist in certain pressure range after the f-delocalization. However, in other light rare earth metals like Neodymium, the alpha-Uranium phase is known to exist at high pressures without any discernible volume collapse.⁵ In trans-plutonium metal like Americium (Am), volume changes by only 2 to 7 % are observed at the pressures identified with f-shell delocalization.⁶ The onset of f-delocalization in rare earth metals and trans-plutonium metals may not always be precisely determined based on the existence of low symmetry crystal structures in high pressure experiments. For example, there is a considerable debate about the f-delocalization in Am, whether it occurs at 10 GPa transition to a γ -plutonium phase or at 16 GPa transition to an orthorhombic P_{nma} phase.⁷ Therefore, precise electrical resistivity measurements are needed to monitor the changes in the electrical properties caused by the availability of extra 4f or 5f electrons that become itinerant at this transition.

Praseodymium (Pr) belongs to the group of light rare earth metals with solid-state electronic configuration of $4f^2$ and $(spd)^3$ with two electrons localized in the 4f-shell and three electrons in the conduction band contributing to a trivalent metallic behavior at ambient conditions. Pr crystallizes in the double hexagonal closed packed (dhcp) structure at ambient conditions. Pr is known to undergo four phase transformations to pressure of 103 GPa at room temperature.⁸ The dhcp phase transforms to face centered cubic phase at 4 GPa, followed by transformation at 6.2 GPa to a distorted fcc phase. These low-pressure transformations between

the close-packed structures in Pr are in large part driven by the electronic s to d transfer⁹ under high pressures within a trivalent electronic state. Two additional transformations to a monoclinic phase at 12 GPa and orthorhombic phase at 20 GPa are also known.⁸ Several of these pressure induced phase transformations have been followed to high temperatures and various triple points in the phase diagram of Pr have been established.^{10,11} It is the last transformation at 20 GPa in Pr which is the most significant as it is accompanied by a large volume collapse and leads to the formation of alpha-Uranium phase.^{12,13} The large volume change and appearance of alpha-Uranium phase are strong indicators of participation of 4f-electrons in conduction band, however, there is no direct electronic evidence of this transition. The contribution of two additional 4f-electrons to the conduction band is expected to substantially increase the electrical conductivity. The electronic changes at the f-delocalization transition in rare earths and actinide metals at high pressures motivate the present study.

The four probe electrical resistance measurements on Pr were performed using designer diamond anvils¹⁴ where tungsten metal probes were patterned using lithographic techniques at the Lawrence Livermore National Laboratory and encapsulated within a chemical vapor deposited diamond layer at the University of Alabama at Birmingham. The electrical probes are only exposed near the center of the diamond for making contact with the sample and elsewhere they are completely insulated within a single crystalline diamond layer. This designer diamond anvil allows us to use metallic gasket for sample containment and for a precise 4-probe electrical resistance measurements. Furthermore, having eight electrical probes gives us the flexibility to measure 4-probe resistance in various regions of the sample for any non-uniformity across the sample. The electrical resistance measurements were made using the Van der Pauw four-probe technique to eliminate the resistance of the probes and other contact resistances in the sample chamber assembly. Five different high-pressure experiments were performed on Pr sample to confirm the reproducibility of the electrical resistance data and ruby fluorescence technique was employed for pressure measurements in all experiments.

Figure 1 shows the photomicrograph of Pr sample in an eight-probe designer diamond anvil at a pressure of 56 GPa. The current and voltage leads are indicated along with the Pr sample of 120 microns in diameter. The constant current source (1 mA) and a nano-voltmeter

were used to measure electrical resistance and the values reported at each pressure are averages of twenty independent readings. It should be noted that measurement probes are embedded in a layer of single crystalline diamond and show no signs of plastic deformation to the highest pressure of 56 GPa. The lack of plastic deformation of embedded electrical microprobes under high pressures allows us to use the ambient pressure probe spacing of 35 microns in converting resistance data to quantitative resistivity values for our sample.

Figure 2 shows the four-probe resistance of Pr-sample as a function of pressure during the compression cycle. In the pressure range of 0 to 20 GPa, there is an overall increase in resistance which can be largely attributed to sample extrusion or thinning and hence a decrease in the cross-sectional area of the specimen. At 20 GPa an abrupt drop of approximately 50 % is observed in a narrow pressure range of 3 to 5 GPa. The resistance reaches a steady state value between 25 to 30 GPa. This drop in resistance coincides with the formation of alpha-Uranium phase in praseodymium as confirmed by numerous x-ray investigations. It should be noted that in addition to this abrupt change at 20 GPa, weaker minima at 6 GPa and 12 GPa are also observed in our data and can be attributed to other structural transformation occurring at these pressures.

Since, the compression data is invariably affected by the sample extrusion and other sample geometry considerations, decompression data can reveal absolute value of sample resistivity. During decompression of the sample there is no sample extrusion and hence appropriate cell constant for the sample can be applied. To relate the measured sample resistances to resistivities, 3-D current flow simulations were performed of the sample and probe geometry. A more detailed description of these current flow simulations can be found in Ref. 15. The measured resistance values were divided by 71.4 to convert to resistivity in Ohm-Cm and are shown in Fig. 3. Again the abrupt change at 20 GPa is apparent and sample resistivity of 70 micro-Ohm cm is consistent with the ambient pressure value for Pr. It is interesting to note that the weak minima at 6 and 12 GPa are still apparent in the decompression data, even though the sample extrusion effects have now been eliminated. Therefore, the first minima at 6 GPa can be assigned to the fcc to distorted fcc phase transition and the second minimum at 12 GPa in Fig. 3

can be assigned to the distorted fcc phase to the monoclinic C2/m phase transition reported in Pr.⁸

Table I summarizes all high-pressure experiments on Pr. The resistance drop both on compression and decompression are documented. During decompression, particularly from extreme pressures (Experiment 3 to 56 GPa), enhanced pressure gradients over the sample regions are observed. This is due to the work hardening of the sample and has the tendency to broaden the observed phase transitions during decompression. The average resistance drop for the five experiments during compression was calculated to be 48 % from Table I. It should be noted that our observed value of resistance drop is consistent with the 50 % drop reported for cerium metal at the f-delocalization pressure of 0.7 GPa.¹⁶

In conclusion, we have observed a drop in electrical resistivity of Pr sample on average of 48 % in the five experiments to 56 GPa at room temperature. This drop in resistivity is attributed to the delocalization of 4f-shell in Pr as f-electrons become itinerant and contributes to electrical conduction at high pressures. In addition weaker anomalies at 6 GPa and 12 GPa attributed to other structural transformations are clearly apparent in the data. Our studies show that the designer diamond four probe technique is ideally suited for studies of f-shell delocalization phenomenon in light rare earth metals and trans-plutonium metals where structural studies may not provide clear evidence of onset of this transition.

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TABLE I. Summary of five experiments on Pr. Experiment number, maximum pressure (P_{MAX}), resistance drop ($\Delta R/R \times 100$) during compression and resistance jump during decompression are shown.

	P_{MAX}	Resistance drop at 20 GPa (Compression)	Resistance Jump at 20 GPa (Decompression)
Experiment 1	32 GPa	52.5%	60.0%
Experiment 2	30 GPa	43.1%	Lost Ruby Signal
Experiment 3	56 GPa	44.0. %	16.9%
Experiment 4	30 GPa	55.6%	Lost Ruby Signal
Experiment 5	30 GPa	45.8%	43.2%

Figure Captions:

Figure 1: Photomicrograph of the Pr sample in an eight-probe designer diamond anvil at a pressure of 56 GPa. The flat size or culet of the designer diamond anvil is 250 microns and Pr sample size is 120 microns in diameter at the center of anvil. The eight probes coming from underneath the diamond lie on a circle of 35 microns in diameter. The direction of the current (I) flow and polarity of the voltage leads are indicated in this four-probe configuration.

Figure 2: Electrical resistance of Pr sample using the four probe measurements during a compression cycle to 32 GPa (Experiment 1). The resistance drop of 52 % at 20 GPa phase transition is indicated. Some weaker anomalies are also observed at structural transformations at 7 and 12 GPa respectively.

Figure 3: Electrical four probe resistivity in micro-Ohm cm during decompression cycle for Experiment 1. The experimental data was converted in to electrical resistivity using the cell constant discussed in the text. The resistance jump during decompression at 20 GPa is clearly evident. The weaker anomalies at 7 and 12 GPa persist during the decompression cycle.

Figure 1

Figure 2

Figure 3