Annual Scientific Progress Report

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Our goals for the first year of this grant were as follows: (a) set up and test a suitable refrigerator; (b) set up a laser and spectrometer fluorescence system to determine the pressure within the diamond anvil cell; (c) perform initial resistivity measurements at moderate pressures from room temperature to liquid helium temperatures (~1K); (d) investigate f-electron materials within our current pressure capabilities to find candidate materials for high-pressure studies. During the past year, we have ordered almost all the components required to set up a diamond anvil cell facility at UCSD, we have received and implemented many of the components that have been ordered, we have performed low pressure research on several materials, and we have engaged in a collaborative effort with Sam Weir at Lawrence Livermore National Lab (LLNL) to investigate Au_4V under ultrahigh pressure in a designer diamond anvil cell (dDAC). The following sections of this report serve to highlight the progress we have made towards developing an ultrahigh pressure research facility at UCSD, the research performed in the past year, as well as future directions we plan to pursue.

1. Ultrahigh Pressure Diamond Anvil Cell Facility

a. Cryogenic Refrigerator

Many f-electron materials exhibit structural, magnetic, and superconducting phase transitions at low temperatures. As a result, a cryogenic refrigerator is necessary to thoroughly investigate many of these f-electron materials. We have chosen and purchased a suitable refrigerator: the Oxford Kelvinox MX100 ^{3}He-^{4}He dilution refrigerator, which is slated for delivery in August 2004. The Kelvinox MX100 will be equipped with a high precision 9T wide bore superconducting magnet and is specified to be capable of reaching a base temperature of 15 mK, a temperature almost two orders of magnitude lower than can be achieved by the cryostat used with our current hydrostatic piston-cylinder cell. The MX100 will also be equipped with a sliding seal to reduce liquid helium consumption, as well as provide quick turnaround time after the insert has been warmed above liquid helium temperatures, an event which will occur regularly with the pressurization of a screw-type DAC. Upon receipt of the refrigerator, an insert will be constructed to support the DAC and feed electrical and optical connections to the DAC.

b. Ruby Fluorescence Pressure Calibration

Pressure calibration in a DAC is usually achieved via ruby fluorescence, wherein a laser is used to excite a pressure-dependent emission line of ruby that is detected using a spectrometer. A typical pressure measurement setup consists of a laser, spectrometer, and microscope, all of which we have acquired or fabricated. The laser that will be used to determine the pressure in a DAC is a Lexel argon laser with a power range of 1mW - 1W. We have purchased and received a CCD camera to be used with a SPEX 500M monochromator. The combination of the CCD camera and the monochromator provides us with a spectrometer capable of recording an entire ruby fluorescence spectrum in one snapshot. The ability to quickly and continuously monitor the pressure in a DAC is imperative, owing to any differential thermal contraction the DAC experiences upon cooling. The spectrometer is computer controlled, which provides instant analysis of the ruby spectrum allowing for precise positioning of the DAC using the intensity of the ruby spectrum. The final element of a room-temperature pressure calibration system is a microscope. We have fabricated a microscope capable of a magnification of 200X, which is necessary due to the extremely small size of the ruby powder used in the DAC. The microscope also includes optics permitting inline illumination from both the laser and any other illumination sources, as well as the appropriate filters and beamsplitters to allow simultaneous viewing by an operator and the spectrometer.

c. Micro EDM

The successful use of a DAC can be very dependent upon the quality of the gasket and thus the sample space used in the experiment. A gasket must be pre-indented and a hole must be drilled in the center of that indent to provide a sample chamber. The drilling of the gasket is extremely important, because burrs or deformations can result in failure of the DAC at relatively low pressures. The preferred technique for preparing the sample chamber of a DAC is to use a micro Electric Discharge Machine (EDM) to electrically cut the hole in the gasket. Using an EDM has two distinct advantages over micro drilling: the drilled holes have no burrs, and the lack of physical contact between the bit and the gasket yields a strong, deform-free chamber. We have ordered a micro EDM from Hylozoic Products, and expect delivery in September 2004. We have purchased and received a Nikon SMZ-660 stereoscopic microscope to align the EDM bit in the center of the indent in the gasket, which is of critical importance to avoid the extrusion of the sample chamber and failure of the DAC.

d. Diamonds

We have purchased six 1/3-carat diamonds for use as diamond anvils. Three of the diamonds were exchanged with Sam Weir at (LLNL) for two designer diamonds with resistivity microprobes and one designer diamond with a multiloop coil to be used for ac susceptibility measurements. A blank diamond and designer diamond make a pair of anvils that can be used in a DAC.

e. Diamond Anvil Cells

We have borrowed a helium gas-pressurized DAC from Sam Weir at LLNL that uses a gas-driven membrane to apply pressure to the diamonds, which permits the pressure in the sample chamber to be adjusted without removal of the DAC from the cryostat. The DAC was prepared at LLNL by a graduate student from UCSD using an electrical resistivity microprobe designer diamond and a blank diamond. The sample chamber of the DAC was loaded with a powdered sample of Au_4V and several ruby chips, after which it was transported to UCSD for low-temperature pressure measurements. Pressure measurements using the gas-pressurized DAC will be limited to temperatures above the freezing point of helium, at which point the helium inside the membrane will no longer transmit the gas pressure to the diamonds. In addition to the gas-pressurized DAC loaned to us, we have intentions to purchase several screw-type DAC's. Since a screw-type DAC uses a piston to apply pressure to the diamonds, it is not constrained by temperature, as are gas-pressurized DAC's, allowing the screw-type DAC's to be used in the dilution refrigerator down to mK temperatures.

2. Pressure Measurements

a. $CeRh_{1-x}Co_xIn_5$

Recently, we have performed hydrostatic pressure measurements on the f-electron material $CeRh_{1-x}Co_xIn_5$ using a piston-cylinder clamp. Pressure measurements up to 28 kbar were made on samples with Co concentrations x = 0.1, 0.2, 0.4, and 0.6. Co concentrations of x = 0.1 and 0.2 display antiferromagnetism at ambient pressure and pressure-induced superconductivity at pressures of 6.9 kbar and 8.8 kbar, respectively. Antiferromagnetism and superconductivity coexist until magnetic order is suppressed toward a QCP at approximately 24 kbar for both concentrations. Samples with Co concentrations of x = 0.4 and 0.6 exhibit ambient pressure superconductivity; however, x = 0.4 shows signs of antiferromagnetism at ambient pressure while one at x = 0.6 shows no signatures of antiferromagnetism in electrical resistivity. For x = 0.4, antiferromagnetism is quickly suppressed toward a quantum critical point at $P_c \sim 6$ kbar, after which superconductivity persists to the highest pressures measured. For x = 0.6, superconductivity exists at ambient pressure and persists to the highest pressures measured. Unlike other heavy fermion compounds where superconductivity exists in a small region surrounding the QCP, $CeRh_{1-x}Co_xIn_5$ exhibits superconductivity over a broad region that is not necessarily centered around the QCP. It was found that all concentrations measured display non-Fermi liquid behavior even to the highest pressures measured, consistent with other heavy fermion materials near a QCP.

b. $PrFe_4Sb_{12}$

We have synthesized and measured single crystals of the filled skutterudite compound $PrFe_4Sb_{12}$, a heavy fermion, weak ferromagnet with an ambient pressure Curie temperature of $T_C = 4.1$ K, as determined by neutron diffraction and modified Arrott plot analysis. A broad peak in the specific heat centered at ~ 4 K, a shoulder in the resistivity data at ~10 K (with an inflection point at T ~ 4.8 K), lack of saturation in M(H), and large value of μ_{eff} / M_{sat} all suggest the presence of an itinerant Fe moment. The electrical resistivity of $PrFe_4Sb_{12}$ has been shown to be very weakly dependent upon magnetic field and pressure. The Curie temperature of $PrFe_4Sb_{12}$ decreases only slightly with applied pressure, evolving from an ambient pressure value of T_C = 4.8 K (defined as the inflection point in the electrical resistivity as a function of temperature) to a minimum value T_C = 3.9 K at the maximum pressure of 23 kbar. A preliminary estimate of the critical pressure at which ferromagnetism is suppressed in $PrFe_4Sb_{12}$ was performed and results suggest a critical pressure of approximately 100 kbar, a pressure well within the range of diamond anvil cell technology.

c. $NdOs_4Sb_{12}$

We have also synthesized and measured another filled skutterudite compound similar to $PrFe_4Sb_{12}$. $NdOs_4Sb_{12}$, like its relative $PrFe_4Sb_{12}$, is a heavy fermion compound with a large $\gamma \approx 435$ mJ/mol-K^2 corresponding to an effective mass $m^* \sim 82\ m_e$. Weak, mean-field-type ferromagnetism was also observed in this compound with an ambient pressure Curie temperature of $T_C \sim 1$ K. Electrical resistivity measurements indicate the presence of both s-f exchange coupling and aspherical coulomb scattering. Low temperature electrical resistivity measurements also suggest the existence of spin-wave excitations below T_C. It was found that the ferromagnetic transition in $NdOs_4Sb_{12}$ increases with pressure up to a value of T_C = 1.8 K at 28 kbar. The pressure dependence of the Curie temperature, however, displays a reduction in the rate of increase indicating the possible existence of a maximum at a pressure of approximately 35 kbar and a subsequent suppression of magnetism for higher pressures.

d. Au_4V

We have measured the electrical resistivity of the ferromagnetic compound Au_4V under hydrostatic pressure up to 25 kbar. The electrical resistivity of Au_4V as a function of temperature displays a characteristic kink corresponding to magnetic ordering in the system at approximately T_C = 45 K. With applied pressure, the Curie temperature of a single crystalline sample increased to a value of T_C = 52 K. A polycrystalline sample of Au_4V was filed into a fine powder and, with our collaborator Sam Weir, loaded into a

DAC at LLNL. High-pressure electrical resistivity measurements were performed on the Au_4V powder at LLNL up to a pressure of almost 200 kbar. Initial results are in excellent agreement with the lower pressure hydrostatic cell data taken at UCSD. The high-pressure diamond anvil studies indicate that the Curie temperature of Au_4V continues to increase to a value of $T_C \sim 90K$ at a pressure of approximately 200 kbar. Above 200 kbar, no resistive transition due to the onset of ferromagnetism could be resolved.

3. Future Directions

We will continue our efforts to establish an ultrahigh pressure facility at UCSD by installing and testing our dilution refrigerator upon receipt, fabricating a cryostat for high temperature measurements from 1 K - 300 K, and integrating our ruby fluorescence system into our cryogenic refrigerators. We plan to purchase the last few items necessary for the success of the ultrahigh pressure facility including screw-type diamond anvil cells for low temperature work, microscopy for aligning diamonds and mounting samples, and depth gauge instruments for determining gasket thickness. We will continue our research into non-Fermi liquid behavior and superconductivity around quantum critical points by measuring new compounds in diamond anvil cells including the heavy fermion skutterudite compounds $PrFe_4Sb_{12}$ and $NdOs_4Sb_{12}$. We plan to investigate Au_4V under high pressure and low temperatures unachievable at the facilities at LLNL to search for the appearance of superconductivity. We also plan to investigate the ac susceptibility of Au_4V in a multiloop designer DAC with our collaborators at LLNL. We plan to perform electrical resistivity and ac susceptibility measurements under pressure on the doped $PrOs_{4(1-x)}Ru_{4x}Sb_{12}$ system in an effort to investigate the two disparate types of superconductivity present at the end members of the doped system. We will also continue our exploratory efforts at searching for new compounds that display quantum critical behavior under pressure, magnetic field, chemical substitution, or a combination of those parameters.

Project Participants

Faculty

Name: M. Brian Maple

Percent Contribution: 10%

Contribution to Project: Research group leader and Principal Investigator.

Post-Doctoral Researcher

Name: Pei-Chun Ho

Percent Contribution: 50%

Contribution to Project: Designs and performs laboratory experiments in collaboration with PI.

Graduate Students

Name: Jason R. Jeffries

Percent Contribution: 100%

Contribution to Project: Prepares intermetallic samples and performs high pressure measurements, responsible for development and implementation of ultrahigh pressure facility.

Name: Nicholas P. Butch

Percent Contribution: 50%

Contribution to Project: Prepares intermetallic samples and performs measurements of magnetic and transport properties of f-electron materials.

Name: Neil A. Frederick

Percent Contribution: 25%

Contribution to Project: Prepares filled skutterudite compounds and performs specific heat, magnetization, and transport measurements on heavy fermion, non-Fermi liquid, and other f-electron materials.

Name: Todd A. Sayles

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Contribution to Project: Prepares intermetallic samples and performs specific heat, magnetization, and transport measurements.

Undergraduate Student:

Name: Stella K. Kim

Percent Contribution: 50%

Contribution to Project: Prepares filled skutterudite and intermetallic compounds.

Publications and Technical Presentations

P. –C. Ho, W. M. Yuhasz, N. P. Butch, N. A. Frederick, T. A. Sayles, J. R. Jeffries, M. B. Maple, "Ferromagnetism and heavy fermion behavior in single crystals of $NdOs_4Sb_{12}$," (in preparation).

J. R. Jeffries, N. A. Frederick, E. D. Bauer, H. Kimura, V. S. Zapf, K. –D. Hof, T. A. Sayles, M. B. Maple, "Electrical resistivity under pressure and specific heat of $CeRh_{1-x}Co_xIn_5$," (in preparation).

N. P. Butch, W. M. Yuhasz, P. –C. Ho, J. R. Jeffries, N. A. Frederick, T. A. Sayles, M. B. Maple, J. B. Betts, A. H. Lacerda, F. M Woodward, J. W. Lynn, P. Rogl, G. Giester, "Ordered magnetic state in $PrFe_4Sb_{12}$ single crystals," (in preparation).

M. B. Maple, P. -C. Ho, J. R. Jeffries, B. J. Taylor, N. A. Frederick, W. M. Yuhasz, T. A. Sayles, N. P. Butch, S. K. Kim, S. T. Weir, A. H. Lacerda, E. D. Bauer, V. S. Zapf, "Fermi Liquid Instabilities and Superconductivity in the Vicinity of Quantum Critical Points in f-electron Materials," Poster Session: National Nuclear Security Administration Stewardship Science Academic Alliances Symposium, March 2004.

J. R. Jeffries, N. A. Frederick, E. D. Bauer, H. Kimura, V. S. Zapf, K. –D. Hof, T. A. Sayles, M. B. Maple, "Superconductivity, Antiferromagnetism, and Quantum Critical Behavior in $CeRh_{1-x}Co_xIn_5$," Poster Session: National Nuclear Security Administration Stewardship Science Academic Alliances Symposium, March 2004.

P.-C. Ho, N. A. Frederick, W. M. Yuhasz, N. P. Butch, M. B. Maple, E. D. Bauer, A. H. Lacerda, V. S. Zapf, "Unconventional Superconductivity and Quadrupolar Ordering in Heavy-fermion Compound $PrOs_4Sb_{12}$," Poster Session: National Nuclear Security Administration Stewardship Science Academic Alliances Symposium, March 2004.

M. B. Maple, “Fermi Liquid Instabilities and Superconductivity in the Vicinity of Quantum Critical Points in f-electron Materials,” Invited Talk: National Nuclear Security Administration Stewardship Science Academic Alliances Symposium, March 2004.