STUDIES OF THE III-V COMPOUNDS IN THE MEGABAR REGIME

Technical Progress Report
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PROGRESS REPORT

X-ray diffraction patterns were obtained using a tapered lead aperture. A detailed analysis of the effect of the tapered aperture is given. Experimental studies include results on W (423 GPa), on Pt (440 GPa, obtained using Type IIa diamonds) and Mo (560 GPa).¹ These results extend earlier studies in which we achieved for the first time static pressures greater than the pressure at the center of the earth (mentioned in last year's report). The cell containing the Mo sample is intact and will be used for higher pressure studies as soon as a 2 μm diameter cylindrical aperture is available, an area in which we are working on hard now. We are currently testing a new design at CHESS. For high energy x-rays the aperture in our high Z material (W) has to be nearly a centimeter long and so the aspect ratio of the aperture will have to be 5000:1. This work is being spearheaded by Qing Xia.

We have on another project made theoretical calculations to show that diamonds with tiny enough tips (flats of 6 μm diameter) may support pressures of 1000 GPa (one terrapascal, 1 TPa). We will need smaller gasket holes to carry on this work and Martin Ettenberg is doing his Senior Thesis (no salary) with me on the use of chemical laser etching to produce such holes.

An important factor in these measurements is the effect of nonhydrostaticity and the x-ray aperture shape, both of which were analyzed in detail.

The results of high pressure studies on graphite were used to model C-60 and to compute the bulk modulus of C-60 molecules and crystals. An important factor in optical studies is the change in the refractive index of the diamond anvil and this was calculated for the first time and shown to result in major dispersive effects reflectivity which is similar to a plasma edge. X-ray studies at high pressures were made on AlP (which appears to become amorphous at 30 GPa), AlAs, InAs, Zr and preliminary results were obtained on GaN.

I. TECHNICAL PROGRESS REPORT ON
GRANT NO. DE-FG02-87ER-45320

"Studies of III-V Compounds in the Megabar Regime"

by A. L. Ruoff

ABSTRACT

In this project we develop techniques for making high pressure measurements (x-ray diffraction and optical measurements) on samples in the multimegabar regime and we make systematic studies of the crystal structure of III-V compounds and other materials as a function of pressure with the broad objective of providing experimental data over a broad range of coordination number and interatomic spacing which can play a leading role in the testing and development of theoretical models of binding.

PROGRESS REPORT

After our monumental breakthrough in 1990 (reaching pressures of 416 GPa as measured by x-ray diffraction, greater than those at the earth's center which is calculated to be 361 GPa) we decided that we might reach still higher pressures. We succeeded in 1991 in reaching pressures of 560 GPa measured by x-ray diffraction on a molybdenum sample. For comparison, one other group has reached a static pressure as high as 305 GPa on several samples. We have now reached pressures of 423 GPa on W and 440 GPa on Pt (the latter using Type IIa diamonds).

Using the Chua-Ruoff scaling relation for the pressure dependence of the compressive flow stress, the effect of the presence of a finite yield strength on the measurement of pressure in a diamond anvil cell by energy dispersive x-ray diffraction is calculated.² Using results from an earlier experiment in which the pressure was found by x-ray diffraction to be 364 GPa (exceeding the pressure at the center of the earth) without this correction, we calculated that the actual pressure lies in the range 378-395 GPa with the correction for nonhydrostaticity being 5-9%.

High-pressure, high-temperature energy-dispersive x-ray diffraction studies were carried out on the group-IV transition-metal zirconium (Zr) to 36 GPa using a synchrotron-radiation source to investigate the entropy contribution in the ω -to-bcc phase transition.³ A room-temperature equilibrium transformation pressure of 35 ± 3 GPa between the ω and bcc phases of Zr metal was observed. A negative slope of 39 ± 4 K/GPa along the ω -bcc phase boundary observed in this experiment gives experimental evidence indicating thermal contribution to the structural sequences in transition metals and shows that the ω phase of Zr metal (a phase of group-IV transition metals) has lower entropy than its pressure-induced bcc phase (isostructural with group-V transition metals). Extrapolation of the present data indicates that the previous observation of a

phase transition in shock-wave experiments at 26 GPa and 540 K is due to this ω -to-bcc phase transition.

The x-ray diffraction data on gold in a gold-zirconium mixture compressed up to 30 GPa have been analyzed using an equation for the lattice strain in the combined presence of uniaxial stress component (USC) and hydrostatic pressure.⁴ The quantity (St) (where $S = \{s_{11}-s_{12}-(1/2)s_{44}\}$ and t is USC) which is obtained from the analysis, increases from 0.0065 at 7 GPa to 0.0075 at 17 GPa. Beyond this pressure, (St) drops drastically, reaching 0.002 at 20 GPa. The drop in (St) is accompanied by a decrease of lattice microstrain. The shear strength of gold at 10 GPa as estimated from these data is 0.4 ± 0.06 GPa.

Pressure studies on graphite were made to 51 GPa. There is a phase transition beginning at 15 GPa to a new phase which is denser and very hard and transparent. We were unable to index this phase because x-ray diffraction from the sample absorbs energy which leads to lower subsequent Compton scattering from the tip of the downstream diamond resulting in dips at that energy in the background. There are many such dips which greatly obfuscate the diffraction pattern (from the low z material) which is also superposed on the Compton scattering background. We are preparing to do angle dispersive diffraction with an image plate to avoid this problem. Our extensive studies on diamond (we have to study the material of our anvils) and these studies on graphite lead us to study the stiffness of

buckyball molecules and C-60 crystals, since to a first approximation one can think of a graphite sheet of 60 atoms folding into a sphere (changing as necessary from only hexagons to hexagons and spheres).

The bulk modulus of an individual C-60 molecule was calculated⁵ in terms of the C,C bond force constant. A range of values for the bulk modulus was obtained with literature values for the force constant. The values obtained all exceed the bulk modulus (441 GPa) of diamond. With a C,C bond force constant equal to that between adjacent carbon atoms in graphite, 7.08 mdyn/Å, a bulk modulus of 903 GPa was obtained. On the basis of a simple composite model it was calculated that single closest-packed C-60 crystals of C-60 will have a bulk modulus of roughly 668 GPa under hydrostatic pressures. The calculated bulk modulus for a single C-60 "buckyball" therefore suggests the possibility that a C-60 crystal could be the most incompressible material known, at a pressure above about 50 GPa.⁶

When optical studies are made on samples in a diamond anvil cell above one megabar the following situation prevails: the light path is 6000 μm of diamond and 2 μm of sample. Studying the sample is somewhat akin to the problem of weighing a man by watching how much a destroyer sinks when he steps on it. The diamond anvils become terribly distorted elastically with diamonds loaded along [100] becoming tetragonal with c/a ratios of about 0.75 at 3 Mbar.

Such distortion changes the optical properties of the diamond so the refractive index in the anvil becomes a function of distance z from the tip along the axis of the diamond and of r , the radial distance from z . Thus a light wave will traverse a path in the z -direction from the diamond table to the diamond tip in a different time along $r=0$ than along $r \neq 0$. The result is that the diamond is a lens system which can cause apparent absorption and can exhibit dispersive reflection.

Using the results of elastic theory for a specific pressure distribution, the state of stress in the diamond anvil was calculated using linear elasticity theory. Using the piezoelectric coefficients of diamond, we have computed approximately the refractive index of the diamond anvil along the axis. It is shown that a large rapid variation of the real refractive index of diamond in the highly stressed region of the tip with a sample having a real refractive index leads to a "ghost plasma edge," i.e. a reflectivity variation with energy in the infrared which has the form of a plasma edge.⁷ Figure 1 shows the reflectivity from a diamond anvil in which a sample having a real refractive index of $n_s = 3.515$ is located between diamonds from which the refractive index is real and varies from 3.515 at the sample to $n_D = 2.414$ at the table according to an Epstein function with $3d = 0.75 \mu\text{m}$

$$n = \left\{ \frac{1}{2} (n_s^2 + n_D^2) - \frac{1}{2} (n_s^2 - n_D^2) \tanh \left(\frac{z - \frac{3}{2}d}{\frac{d}{2}} \right) \right\} \frac{1}{2}$$

Figure 1. Reflectivity variation with energy for a sample between two diamonds as noted in text.

A steep gradient in n as assumed could be created by the solution of hydrogen in diamond although the gradient due to stress may not be so large unless the nonlinear photoelastic coefficients are quite large, which they might be considering the distortions.

Several different samples of AlP have been prepared and studied at CHESS. All samples have exhibited the expected zinc-blende structure at ambient and low pressures. However, at a pressure of about ~30 GPa, there is apparently a phase transition since the diffraction pattern suddenly becomes a single line. The diffraction pattern is essentially featureless with the exception of one line,

therefore we currently hypothesize that AlP may become amorphous above 30 GPa.

X-ray studies at CHESS have demonstrated that AlAs exhibits the zinc-blende structure at low pressures, and the zinc-blende structure has been convincingly indexed to pressures up to 20 GPa. At ~20 GPa a phase transition occurs, and the diffraction pattern contains in excess of 20 diffraction lines. The crystal structure of this new phase remains undetermined despite several serious attempts to index the diffraction patterns. Our next step is to use angle dispersive diffraction.

We now have an excellent sample and have indexed the low pressure phase of GaN to the wurtzite structure. At a pressure of ~13 GPa (according to the theoretical equation of state) we observed a phase transition and a significant drop in pressure upon increasing the cell load. Preliminary attempts to determine the structure of the new phase indicate that it is hexagonal, and that it may be the NiAs structure. Analysis of this phase is currently in progress.

PUBLICATIONS

1. Arthur L. Ruoff, Hui Xia and Qing Xia, "X-ray Diffraction Studies on Three Samples with a Maximum Pressure of 560 GPa," Cornell Materials Science Center Report #7315, submitted for publication.
2. Arthur L. Ruoff, Huan Luo, Hui Xia and Yogesh K. Vohra, "The Effect of Nonhydrostaticity on Measuring the Pressure in Metals by Energy Dispersive X-ray Diffraction in the Diamond Anvil Cell," High Pressure Research 6, 183 (1991).
3. Hui Xia, Arthur L. Ruoff and Yogesh K. Vohra, "Temperature Dependence of the ω -bcc phase transition in zirconium metal," Phys. Rev. B 44, 10374 (1991).
4. Anil K. Singh, Kalyani Vijayan, Hui Xia, Yogesh K. Vohra and Arthur L. Ruoff, "Uniaxial Stress Component in Au in Au-Zr mixture Compressed up to 30 GPa," to be published in the Proceedings of the XIII AIRAPT Conference, held in Bangalore, India, Oct. (1991).
5. Rodney S. Ruoff and Arthur L. Ruoff, "Is C₆₀ Stiffer than Diamond?" Nature 350, 663 (1991).
6. Rodney S. Ruoff and Arthur L. Ruoff, "The Bulk Modulus of C₆₀ Molecules and Crystals: A Molecular Mechanics Approach," Appl. Phys. Lett. 59, 1553 (1991).
7. A. L. Ruoff and Huan Luo, "Refractive Index in a Loaded Diamond Anvil: Ghost Plasma Edges," Cornell Materials Science Report #7270, to be published in the Proceedings

of the XIII AIRAPT Conference, held in Bangalore, India,
Oct. (1991).

II. CONTINUATION DOCUMENT ON

Grant No. FG02-87ER-45320

"Studies of III-V Compounds in the Megabar Regime"

SUMMARY OF PROGRESS

A. Multimegabar Pressures

Using microminiaturization, we obtained static pressures of 560 GPa.

B. Nonhydrostaticity and Pressure Measurement

We have developed an equation for the effect of nonhydrostaticity on pressure measurement. Using the DAC as usual, this correction increases the pressure.

C. Graphite and C-60

We have studied graphite to 51 GPa. There is a new phase formed at 15 GPa. Although we have not yet obtained a definitive structure for this phase, the extremely small variation of the d-spacings with pressure suggest it is stiffer than diamond. Theoretical studies on C-60 suggest that the buckyball is twice as stiff as diamond and that the C-60 crystal will at high pressures (if it does not decompose) become stiffer than diamond.

D. Dispersive Reflectance from Diamond-sample Interface Due to Refractive Index Variation in Diamond

Experiments on AlP have shown that it becomes amorphous at 30 GPa. Experiments on both AlAs and InAs by EDXD have led to complex patterns for which the structure is not known. Angle dispersive studies will be used in the future in such situations. We have an excellent GaN sample and experiments are underway at CHESS.

RATIONALE FOR RESEARCH

Ultrapressures can cause either large changes in interatomic spacings, changes in coordination number or both. We propose to carry out systematic studies of the crystal structure changes of the III-V compounds as a function of pressure as well as to determine their equation of state and to continue studies on diamond.

The broad objective of the proposed research is to provide experimental data over a broad range of coordination number and interatomic spacing which can play a leading role in the testing and development of theoretical models.

SUMMARY OF PROPOSED RESEARCH

Crystal Structure and Equation of State Studies

In our earlier studies we showed that Sn and InSb (once metallic) had identical equations of states $V(P)$ [not just V/V_0 vs. P]. We propose to study the isoelectronic sequence

to find if this behavior persists. This is not just a simple equation of state study since a number of new crystalline transitions are likely to occur. We propose to extend our studies on Sn to 110 GPa to 250 GPa on InSb from 30 GPa to 250 GPa and to make studies on CdFe and AgI to 250 GPa. We propose to carry out x-ray diffraction studies on InSb, AlAs and InAs using angle dispersive studies. We propose to extend our studies now underway on GaN to 2.5 Mbar using different cells with a smaller tip.

Techniques and Apparatus Improvement

In our 560 Mbar development we used diamonds with flats with a diameter of 20 μm and we used a sample hole with a diameter of 10 μm . In pushing to even higher pressures further microminiaturization is needed. We have found previously that

$$P_{\text{max}} \text{ (GPa)} \propto D \text{ (}\mu\text{m)}^{-1/2}$$

where D is the flat diameter. If this behavior persists to higher pressures a tip with $D = 6 \mu\text{m}$ will be needed to reach 1000 GPa (1 TPa). The latter would require making a 3 μm sample hole and a 2 μm collimator hole.

Martin Ettenberg, a Senior MS&E student is working to create these small gasket holes by laser enhanced chemical etching. In the iron or rhenium gasket this means 3 μm holes in a 20 μm thick preindented gasket. Here the centering of the hole on the flat is very important. At the same time we require an x-ray collimator with a 2 μm diameter cylindrical aperture in a high Z sheet such as W up to 7000 μm thick. These are major challenges. A major effort is underway on this and an aperture with a length of 2000 μm is now being tested at CHESS.

One of the important factors of transitions at high pressure is the effect of nonhydrostaticity. We now have a system for loading gases into a DAC containing a solid sample. This provides a convenient way of loading argon or Neon as a pressure medium so our studies can be carried out on a sample under quasi-hydrostatic conditions. In our previous studies on argon with a CsI sample we also obtained superb diffraction patterns from argon, which leads us to believe that properly calibrated, Argon will be used in some experiments for both the pressure median and the x-ray marker for measuring pressure.

We expect that by the end of the second year of this program we will have carried out angular dispersive diffraction using image plates to achieve higher resolution than with EDXD, and will have this available as a routine tool at CHESS.

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