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STUDIES OF THE III-V COMPOUNDS IN THE MEGABAR REGIME

Annual Technical Progress Report for Grant No. DE-FG02-87E745320

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PROGRESS REPORT--SYNOPSIS

The Bridgman Medal was awarded to Prof. A. L. Ruoff. A 5 μm x-ray aperture for studies to 100 keV at CHESS was developed and a procedure was developed to measure accurately the aperture size.

It was shown that all the compounds AlN, GaN and InN transform to the Cl-type structure with AlN nitride remaining as 100% rocksalt structure on release of pressure. Various parameters in the EOS were measured.

The EOS of BP was measured to 110 GPa but no phase transitions were seen.

AlAs was shown to transform from the initial zincblende phase to the nickel arsenide phase, the first case of this in the IV-V compounds.

Our first experiments on CdTe were carried to 51 GPa and are now being analyzed.

It was an exciting year and we expect to have a great year in 1994.

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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. We also create new materials.

PROGRESS REPORT

Prof. A. L. Ruoff was awarded the 1993 Bridgman Medal for his outstanding high pressure research. The Bridgman medal is awarded biannually at the meeting of the International High Pressure Association (AIRAPT). This is mentioned here because the Department of Energy played a major role in supporting his work (including when it was called the AEC).¹

Following our reaching pressures of 560 GPa (and over 400 GPa in three materials: Mo, 560 GPa; Pt, 440 GPa; W, 423 GPa) it became clear that we required for our x-ray studies an aperture system which produces a very tiny x-ray beam. We have succeeded in making a square aperture with a 5 μm edge and moreover we have developed a sophisticated metrology which proves that we indeed have such an aperture.² A brief summary of this was reported at the AIRAPT meeting in Colorado Springs in June.³ It is intended that we will make 2 μm apertures for use at the new 24-pole wiggler at CHESS and with 10 μm diameter or smaller diamond tips.

We have made extensive transition studies on the three nitrides AlN ,⁴ GaN ⁵ and InN ⁶ and our findings will be briefly discussed here. See Table 1 on the next page. We see the onset of transformation in AlN ⁴ from the wurtzite structure to the 6-fold NaCl structure at 14 GPa, a structure which persists to 65 GPa. The equation of state

Table 1. Summary of results.*

	Experiment	Theory
AlN		
P_t (GPa)	0-14	12.9
$V_o(r)/V_o(w)$	0.81 ± 0.02	-
$(V_I - V_{II})/V_I$	18.6%	-
Wurtzite		22.5%
Bo (GPa)	187 ± 5.0	
Bo'	5.5 ± 1.0	3.74
Rocksalt		
Bo (GPa)	222 ± 5.0	215.0
Bo'	4.8 ± 1.0	4.58
GaN		
P_t (GPa)	30-37	55
$V_o(r)/V_o(w)$	0.83 ± 0.02	-
$(V_I - V_{II})/V_I$	17.0%	15.8%
Wurtzite		
Bo (GPa)	188 ± 5.0	179
Bo'	3.2 ± 1.0	3.93
Rocksalt		
Bo (GPa)	248 ± 5.0	244
Bo'	5.5 ± 1.0	-
InN		
P_t (GPa)	5-10	-
$V_o(r)/V_o(w)$	0.81 ± 0.02	-
$(V_I - V_{II})/V_I$	20.0%	-
Wurtzite		
Bo (GPa)	144.0 ± 5.0	-
Bo'	4.07 ± 0.5	-
Rocksalt		
Bo (GPa)	163 ± 4.0	-
Bo'	3.3 ± 0.5	-

* Here V_o is the atomic volume at zero pressure, V_I and V_{II} are the atomic volumes just before and just after phase transition, w and r mean respectively the wurtzite structure and the rocksalt structure.

for both phases is obtained. The high pressure form persists as a metastable phase on unloading to atmospheric pressure. Thus a new material has been created. The theoretical calculated transition is at 12.9 GPa, while experimentally we can only say that $0 \leq P_t < 14$ GPa. The experimental volume change at 14 GPa is 18.6% whereas theoretically (ab initio pseudopotential) it is 22.5% at 12.9 GPa.

The bulk modulus at zero pressure for the new AlN material is 222 ± 5 GPa compared to the value of 187 ± 5 GPa for the wurtzite phase, a 19% increase in stiffness. The results for the three materials were summarized in a brief paper at the AIRAPT meeting in Colorado Springs in June.⁷

In the case of InN some of the high pressure phase persists at atmospheric pressure so that it is possible to directly measure the lattice parameter at zero pressure of the high pressure phase in each case. It compares well to the value obtained from fitting the P-V curve during loading to obtain V_{OR}/V_{OW} and computing a_{OR} from V_{OR} .

In the case of GaN there is a substantial discrepancy between the experimental P_t where $30 < P_t < 37$ and the theoretical value. It will be of interest to see if this discrepancy persists in InN where calculations remain to be done. The Group III nitrides have high commercial interest. There is a major effort on GaN because its large bandgap will make it a useful near ultraviolet detector and

because it can be a high energy laser. AlN, of course, has an extremely high piezoelectric coefficient.

Equation of state measurements were made on the low Z material BP for the first time and these were successfully carried to 110 GPa. This yielded a bulk modulus of 152 GPa slightly lower than the computed value of 165 GPa. This experiment ended short of the 140 GPa recently calculated for the transition pressure. We expect to go for higher pressures in this low Z material. A brief summary of these results was presented at the AIRAPT meeting in Colorado Springs.⁹

The initial studies on AlN were the first (and only the low pressure part) on the isoelectronic series.

Based on studies on another project where x-ray diffraction studies on Al were successfully made to 216 GPa, we now believe that we can make similar studies to compare the EOS of these isoelectronic materials to above 2 Mbars. To a first approximation we expect identical molar-volume versus pressure results.

AlAs was studied in the pressure range 0-52 GPa with both uploading and downloading data obtained last week. In order to overcome earlier problems with reactivity this specimen was loaded in a drybox (which we use to load the

highly active alkali hydrides on another project). An excellent zincblende pattern was obtained at low pressure. A phase transition occurred at 11.9 GPa on loading. Ray Greene has completed the analysis of the data and has found that the high pressure phase has the 6-fold NiAs structure. This is the first NiAs structure found in the III-V compounds. After loading to 52 GPa and then unloading, there is no sign of the zincblende phase reappearing at 4 GPa. However, zb peaks do reappear at 2 GPa. Thus the equilibrium transformation is $2.0 < P_{t \text{ eq}} < 11.9$ or $P_{t \text{ eq}} = 7 \pm 5$ GPa. The ab initio pseudopotential based calculation gives 7.6 GPa. Thus it is clear that other techniques have to be used to determine $P_{t \text{ eq}}$ accurately. We will discuss this further in the proposal section.

We have begun studies on CdTe as part of our studies on the isoelectric series.

We note that our earlier studies on this project showed that once InSb transformed to a metal the V-P curves coincided to high pressure. We have just completed a low pressure experiment to 51 GPa. (The only recent study on CdTe went to 40 GPa.) Hence we are checking these earlier results. The data is currently being analyzed by Ting Lee.

PUBLICATIONS

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2. A.L. Ruoff, H. Luo, C. Vanderborgh, H. Xia, K. Brister and V. Arnold. "The Production and Metrology of 5 μm x-ray Aperture for 100 keV Diffraction Studies in the Diamond Anvil Cell," accepted for publication, Rev. Sci. Instrum. expected Dec. 1993.
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7. Q. Xia, H. Xia and A.L. Ruoff, "New High Pressure Phases of the III-V Compounds AlN, GaN, InN," in "High Pressure Science and Technology 1993," edited by S. Schmidt, George Samara, J.W. Shaner and Marvin Ross, to be published by the American Institute of Physics, May (1994).
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9. H. Xia, Q. Xia and A.L. Ruoff, "Equation of State of BP to Megabar Pressures," in "High Pressure Science and Technology 1993," edited by S. Schmidt, George Samara, J.W. Shaner and Marvin Ross, to be published by the American Institute of Physics, May (1994).

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