

# RESEARCH CONTRIBUTIONS AND SCIENTIFIC ACHIEVEMENTS OF ARTHUR L. RUOFF

While Ruoff was working on his thesis research with Henry Eyring, Prof. Peter Gibbs (who did high pressure science) introduced him to Percy Bridgman's book which included studies of equation of state, phase transitions, mechanical properties, etc., to pressures of up to 78 kb (7.8 GPa) when corrected by Harry Drickamer, George Kennedy and others.

## I. High Temperature Creep of Metals

HTC of metals is controlled by bulk diffusion. Measurements of the pressure dependence of HTC yield the activation volume for self-diffusion,  $\Delta V_{SD}$ . Ruoff's group was the first to do this and did it in an ingenious way by pressure cycling, so they obtained as many as twenty independent values from one sample. Their study on *Al* was especially significant as  $\Delta V_{SD}$  was found to be greater than the atomic volume:  $\Delta V_{SD} = 13.6 \pm 0.6 \text{cm}^3/\text{mole}$  compared to the molar volume of  $9.97 \text{cm}^3/\text{mole}$ . For several other metals studied by the Ruoff group,  $\Delta V_{SD}$  is about 2/3 of the molar volume.

B.M. Butcher, H. Hutto and A.L. Ruoff. Activation Volume and Energy for Self-Diffusion in Aluminum. *Applied Phys. Lett.*, **7**, 34 (1965).

• *As a result of theoretical studies by Ashcroft, Ruoff realized that the pseudopotential for Al was different than for other metals and studied Al because of this, which is why we have the interesting result that the activation volume for self-diffusion in Al is LARGER than the atomic volume (by the factor 1.36).*

Later pseudopotential calculations confirmed the result.

## II. Pressure Dependence of Yield Stress

Percy Bridgman, who won the Nobel Prize for his extensive research on high pressure (up to an actual 7.8 GPa) had attempted to measure the pressure dependence of the yield stress of steel but was unable to observe an effect. Ruoff who had taught the first dislocation course at Cornell knew that in an elastically isotropic solid (which could be an equiaxed polycrystalline aggregate of randomly oriented crystals having any symmetry) the yield stress  $\sigma_0$  at zero pressure,  $\sigma_0(0)$ , is proportional to  $G$  (the shear modulus) if the process is controlled by screw dislocations, or to  $G/(1 - \nu)$  where  $\nu$  is the Poisson ratio if controlled by edge dislocations. In the first case

$$\sigma_0(P) = \sigma_0(0)[G(P)/G_0],$$

where  $G_0$  is the shear modulus at zero pressure. With

$$G(P) = G_0 + G'_0(P), \text{ so that } \sigma_0(P) = \sigma_0 G_0(1 + G'_0 P/G_0).$$

Because  $G'_0$  was in the neighborhood of 1.5 for metals and to make it easier to find an effect, Ruoff studied a metal with a much smaller  $G_0$ . In fact, the experiment showed that the scaling factor  $[G/(1 - \nu)]/[G_0(1 - \nu_0)]$  fitted the data best, showing that the motion of the edge dislocations is the controlling factor.

J.O. Chua and A.L. Ruoff. Pressure dependence of the yield stress of potassium at low homologous temperature. *J. Appl. Phys.*, **46**, 4659 (1975).

Hence

$$\sigma_0(P) = \sigma_0 F(P)$$

where  $F(P)$  was called the *pressure strengthening factor* by Ruoff.

In later years, Ruoff, Christensen and Rodriguez collaborated to obtain  $F(P)$  theoretically to above the 1 TPa range for *Mo* and *W*.

N.E. Christensen, A.L. Ruoff and C.O. Rodriguez. Pressure Strengthening: A way to multi-megabar pressure. *Phys. Rev. B*, **52**, 9121 (1995).

A.L. Ruoff, C.O. Rodriguez and N.E. Christensen. The elastic moduli of tungsten to 15 Mbars, phase transition at 6.5 Mbar and rheology to 6.5 Mbar. *Phys. Rev. B*, **58**, 2998 (1998).

At 550 GPa,  $F(P) = 4.5$  for  $W$ . Without the pressure strengthening factor metal gaskets could not contain the huge multimegabar static pressures attained.

- *The pressure strengthening of the gasket material first suggested by Ruoff and then proven experimentally by his group has enabled multimegabar pressures to be reached and is expected to make it possible to reach pressures over 1 TPa.*

### III. Pressure Dependence of the Elastic Behavior of Liquids and Solids

Ruoff has contributed substantially to the understanding of the elastic behavior of materials at high pressure. This includes elastic studies in which his group made highly accurate studies of the pressure dependence of the bulk modulus of two liquid metals and 25 solids. His group was the first to measure  $d^2c_{ij}/dP^2$  values (on sodium) and hence to provide accurate values of the coefficients of its bulk modulus,  $B_0$ ,  $B'_0$  and  $B''_0$ .

P.S. Ho and A.L. Ruoff. Analysis of Ultrasonic Data and Experimental Equation of State of Sodium. *J. Phys. Chem. Solids*, **29**, 219 (1968).

These coefficients along with the Birch (winner of the Bridgman Award in 1983 for high pressure studies) equation of state provide an accurate  $P(V)$  to high pressures.

- *The measured pressure derivatives of the elastic constants of many materials by Ruoff's group provided a trove of data for theorists developing algorithms to make quantum mechanical calculations accurate with finite computational capacity.*

#### IV. Direct Length Measurements and the Invention of a New Absolute Pressure Gauge Concept with Implementation

Direct volume measurements or length measurement also can be used to measure

$$B_0^T = -V(dP/dV)_T = -(\ell/3)(dP/d\ell)_T$$

(for a solid with an isotropic linear compressibility). Ultrasonic measurements give  $B_0^S$  (constant entropy) at zero pressure and a small measurable correction gives  $B_0^T = B_0^S/(1 + \Delta)$ . Ruoff realized that an absolute pressure gauge could be based on simultaneous length measurements on say a silicon crystal and the appropriate ultrasonic transit times in silicon crystals. A system was designed for this purpose. A meter long single crystal in a pressure vessel was used for length measurements accurate to  $0.03\mu m$ . A connected parallel pressure vessel had three crystals of silicon for transit time measurements. These pressure vessels were in a temperature bath controlled to 0.01C in a room controlled to 0.1C.

R.C. Lincoln and A.L. Ruoff. Absolute Length Measurements at High Pressure. *Rev. Sci. Instrum.*, **44**, 1239 (1973).

The system was used to determine the freezing pressure of mercury of  $7571.2 \pm 1.6$  kb. Values obtained by other groups based on the use of the "free-piston" gauge are:  $7565.4 \pm 3.7$ ,  $7569.2 \pm 1.2$  and  $7571.0 \pm 1.2$ .

A.L. Ruoff, R.C. Lincoln and Y.C. Chen. High pressure calibration with a new absolute-pressure gauge. *Appl. Phys. Lett.*, **22**, 310 (1973).

C-S. Zha, a former operator at CHESS and a friend of Ruoff, later used this concept 27 years later to make absolute pressure measurements to 50 GPa using Brillouin scattering and X-ray based lattice-parameter measurements at CHESS.

- *Ruoff's invention of a totally new pressure-gauge concept (with synchrotron radiation sources as they now exist or are on the horizon) could become the penultimate way of calibrating static pressure scales in the TPa range.*

## V. Development of a Purely Thermodynamic Method of Converting Hugoniot Equations of State to Isotherms

In dynamic shock experiments using explosives or gas-gun loading two quantities are measured: the shock-front velocity,  $u_s$ , and the velocity of the particle after the front has passed,  $u_p$ . These give the well-known three Hugoniot relations. It is found experimentally that  $u_s$  vs.  $u_p$  is nearly a linear relationship with a small quadratic term:  $u_s = c + su_p + s'u_p^2$ . Ruoff showed that the values of  $c$ ,  $s$  and  $s'$  and the Hugoniot relations could be used to obtain the adiabatic coefficients:  $B^S(P) = B_0^S + B_0^{S'} P + B_0^{S''} P^2/2$ .

A.L. Ruoff. Linear shock-velocity particle-velocity relationship. *J. Appl. Phys.*, **38**, 4976 (1967).

Using the thermodynamic relationships of Cooke, Ruoff obtained  $B_0^T$ ,  $B_0^{T'}$  and  $B_0''$ . Morris Keeler tells the story that when he introduced Ruoff to Andre Sakarov, perhaps the greatest shock experimentalist and the inventor of the USSR atomic bomb and hydrogen bomb.

*Sakarov said to Ruoff, "so **you** discovered the thermodynamics approach to get the isotherm from the  $u_s(u_p)$  relation. We are using that to get isotherms from Hugoniots."*

## VI. Creation of the High Pressure Beam Line at CHESS (Cornell High Energy Synchrotron Source)

Ruoff designed and with the help of his able machinist, Volker Arnold (trained in Germany) built the first pressure stage at CHESS (available for inside and outside users). His group made major contributions to the study of EOS of solids from lattice parameter measurements as well as finding new crystal structures caused by pressure. The high quality of their diffraction studies is illustrated in the 1986 studies on *CsI* which transforms from the cubic *CsCl* or *B2* structures to tetragonal and then orthorhombic.

Y.K. Vohra, K.E. Brister, S.T. Weir, S.J. Duclos and A.L. Ruoff. *Science*. **231**, 1136 (1986). This was a generation ago.

• *Numerous X-ray diffraction studies of EOS and phase transition pressures were very useful to theorists who were developing techniques and algorithms which would make, in time, quantum mechanics a quantitative predictor of the solid state as shown by a joint paper with Marvin Cohen's group which resulted after it was learned that they had independently completed work on this problem.*

Y.K. Vohra, K.E. Brister, S. Desgreniers, A.L. Ruoff, K.J. Chang and M.L. Cohen. Phase-transition studies of Germanium to 1.25 MBars. *Phys. Rev. Lett.*, **56**, 1944 (1986).

## VII. Creation of the Field of Multimegabar Research (at Static Pressures)

In 1987, the Ruoff group obtained X-ray data at 216 GPa on rhenium ( $V/V_0 = 0.734$ ) with 12 peaks with  $a = 2.491 \pm 0.003A$  and  $c = 4.020 \pm 0.005A$ .

Y.K. Vohra, S.J. Duclos and A.L. Ruoff. High-pressure X-ray diffraction studies on rhenium to 216 GPa (2.16 Mbars). *Phys. Rev. B*, **36**, 9790 (1987). This work was complemented by their 1988 study of rhenium to 255 GPa.

Y.K. Vohra, S.J. Duclos and A.L. Ruoff. Static Pressures of 255 GPa (2.55 Mbar) by X-ray diffraction: Comparison with extrapolation of the ruby pressure scale. *Phys. Rev. Lett.*, **61**, 574 (1988).

- *In both of the above experiments and several others detailed pressure profiles were measured by Ruoff's group.*

This was followed in 1990 by the comparison (from lattice parameter measurements) of the simultaneously determined  $P$  vs.  $V$  for  $Pb$ ,  $Mo$  and  $Pt$  (all of which had isotherms derived from Hugoniot) to 278 GPa.

Y.K. Vohra and A.L. Ruoff. Static Compression of Metals  $Mo$ ,  $Pb$  and  $Pt$  to 272 GPa: Comparison with Shock Data. *Phys. Rev. B*, **42**, 8651 (1990).

Then came the study of  $Si$  to 248 GPa in which it was shown that  $Si$  transforms to the  $fcc$  structures at  $79 \pm 2$  GPa which persists to 248 GPa ( $V/V_0 = 0.361 \pm 0.006$ ). Earlier predictions of the  $fcc$  phase provided a test of three different theoretical calculations (GPT, LMTO and AP) of the transition pressure and the volume.

S.J. Duclos, Y.K. Vohra and A.L. Ruoff. Experimental study of the crystal stability and equation of state of  $Si$  to 248 GPa. *Phys. Rev. B*, **41**, 12021 (1990).

Also in 1990 it was shown that the secondary absorption edge of diamond dropped from  $3.7eV$  at 1 atm to  $3eV$  at 300 GPa and  $2.5eV$  at 364 GPa.

Y.K. Vohra, H. Xia, H. Luo and A.L. Ruoff. Optical properties of diamond at pressures of the center of the earth. *Appl. Phys. Lett.*, **57**, 1007 (1990).

In 1990 by *miniaturization* of the flat tip diameter to  $21\mu m$  with an  $8\frac{1}{2}$  degree bevel and the collimated X-ray beam diameter to  $4\mu m$ , Ruoff et al., reached 378 GPa in tungsten and



416 GPa in molybdenum, easily surpassing the pressure at the center of the earth of 361 GPa. A pressure profile to 364 GPa was measured.

- Ruoff *et al.*, had surpassed Bridgman's highest pressure, 7.8 GPa (corrected) by a factor of 50.

A.L. Ruoff, H. Xia, H. Luo, and Y.K. Vohra. Miniaturization techniques for obtaining static pressures comparable to the pressure at the center of the earth: X-ray diffraction at 416 GPa. *Rev. Sci. Instrum.*, **61**, 3830 (1990).

In 1991, a pair of Type-IIa diamonds were used to generate a pressure of 338 GPa, showing that the strength of diamond depends primarily on crystal perfection.

A.L. Ruoff, H. Luo, C.A. Vanderborg and Y.K. Vohra. Generating near-earth-core pressures with type-IIa diamonds. *Appl. Phys. Lett.*, **59**, 2681 (1991).

Finally, in 1992 a static pressure of 560 GPa was obtained.

A.L. Ruoff, H. Xia and Q. Xia. The effect of a tapered aperture on X-ray diffraction from a sample with a pressure gradient: Studies on three samples with a maximum pressure of 560 GPa. *Rev. Sci. Instrum.*, **63**, 4342 (1992).

Einstein's following quote is one of Ruoff's favorites. When asked what his research philosophy was, Einstein said, "I don't saw sawdust."

In all the Ruoff group experiments discussed so far the pressure vessel used was a large, stiff pressure vessel in which the long piston and cylinder weighed 52oz. (BIG BERTHA) which was machined at the high precision machining research laboratory at NASA. When others used a tiny compliant vessel (piston and cylinder) weighing only 13 oz. (BABY BERTHA) they have only reached a pressure somewhat over 300 GPa. Ruoff notes the following analogy. In Australia they have huge semi-trailer-tractors (powered by liquid natural gas (LNG)) which pull a "train" of three trailers each with a load of 55 tons down a highway at 60<sup>+</sup> MPH. Could a U.S. semi-tractor which pulls a single trailer with a 40-ton load pull the Australian train at 60<sup>+</sup> miles per hour?

## VIII. Pioneering Studies of the Basis for Reaching Higher Pressures

On the road to pioneering multimegabar research and with the purpose of reaching TPa pressures Ruoff has studied five areas:

1. The design of the pressure vessel.
  - *Ruoff knew that a large diameter piston and a larger thick-walled cylinder allowed machining that leaves a small gap and hence less tilt and that a longer piston cylinder contact also decreases tilt.*
2. The diamonds (how to determine diamonds of the highest perfection). What really matters (absolute perfection), Types IIa. **The presence of a dislocation in the high stress region near the tip is lethal if one is dealing with a chemical (such as hydrogen) which diffuses rapidly down dislocation pipes.**
3. Pressure strengthening of the gasket and the diamonds.
4. Optimum shape design of the diamonds.
5. Microminiaturization.

### Optimum Design

The first paper related to diamond design was simple but very helpful. It led to a triangular pressure profile,  $P = P_M(1 - r/a)$  if the yield stress was constant.

K.S. Chan, T.L. Huang, T.A. Grzybowski, T.J. Whetten and A.L. Ruoff. Pressure concentrations due to plastic deformation of thin films or gaskets between anvils. *J. Appl. Phys.*, **53**, 6607 (1982).

Not bad, but not quantitative. See the measured pressure profiles in Fig. 2 of Vohra, Duchos, Brister and Ruoff, PRL **61**, 1988. Many of the papers listed in Section VII also show measured pressure profiles.

- *Ruoff initiated systematic theoretical studies of the effect of the diamond tip profile and the gasket [including finite non-linear elasticity of the diamonds and plasticity of the gasket, with the “pressure strengthening factor” noted earlier and extensive related experimental results on pressure profiles were obtained].*

H. Poon, A.L. Ruoff and S. Mukerjee. "Optimal Design of Diamond Anvils Using Finite Element Analysis and Simplified Equilibrium Equations. *Inverse Problems in Engineering*, **2**, 20 (1996).

A.L. Ruoff, H. Poon and S. Mukerjee, *Optimal Design in High Pressure Science and Technology*, [Proceedings of AIRAPT XV and EHRPG33 Conference] ed. by W. Trzeciakowski, World Scientific, Singapore (1996) p. 25.

These studies, a "Tesla approach" for attaining ultra pressure, extended what had often been an "Edisonian approach." The application of the plasticity theory in the paper with Poon and the strengthening factor from *Mo* with Christensen in Section II enabled the calculation of the final gasket thickness at  $r = 0$  of  $2.2\mu m$  in *Mo* at 416 GPa. Ruoff has plans to measure thickness in the metals in the future by X-ray absorption and is carrying out a full plasticity analysis with faster computers now that his book, *The Declaration of Energy Independence*, is in press.

### **Microminiaturization**

One of Ruoff's most important discoveries related to getting ultrapressures in the diamond anvil cell is found in Fig. 3 of H. Xia, H. Luo and A.L. Ruoff. Miniaturization techniques for obtaining static pressures comparable to the pressure at the center of the earth: X-ray diffraction at 416 Gpa. *R.S.I.*, **61**, 3830 (1990).

In this case luck had fallen into Cornell's and Ruoff's laps. His group had placed indigitated metal electrodes on a diamond tip, using lithographic techniques, for two-lead resistance measurements.

D.A. Nelson, Jr. and A.L. Ruoff. *PPL* **42**, 383 (1979).

This was one of several non-electrical engineering applications which helped Cornell get the National Submersion Facility (now Cornell Nanoscale Facility). After Edward Wolf became the Director of the former, Ruoff became the Program Committee Chairman and became aware of many of the capabilities in this area. Subsequently, his group in cooperation with other groups, made some extremely important pioneering advances in this area. Originally, sample holes in gaskets were made with carbide drills and a special drill press down to about  $50\mu m$  in gasket materials, *W*, *Mo*, etc., Ruoff initiated drilling them with ion beams with the help of Jon Orloff.

J. Orloff, C. Narayana and A.L. Ruoff. Use of focused ion beams for making tiny sample holes in gaskets for DAC. *Rev. Sci. Instrum.*, **II**, 216 (2000).

The initial holes were  $17\mu m$  in diameter. In cooperation with former postdoctoral associate Gary Stupian,  $4\mu m$  diameter sample holes have been made. It should be noted that it is expected to use these at Grenoble where the beam diameter is  $1.8\mu m$ .

Another impressive micro-miniaturization feat is shown in the following:

A.L. Ruoff, L. Sun, S. Natarajan, C-Z. Zha and G. Stupian. Techniques for X-ray markers at high pressure in the DAC. R.S.I., **76**, 036102-1 (2005).

Here a tiny narrow strip of  $Pt$   $\frac{1}{2}\mu m$  thick, was sputtered on the cylindrical wall of an ion-beam produced hole. Four or even six different strips could have been easily made. This can be achieved with smaller gasket holes.

• *While Janieson and others introduced miniaturizing with the diamond anvil cell, (relative to piston-cylinder devices), Ruoff took it another giant step further with the introduction of microminiaturization, which, he has calculated will lead to TPa static pressure.*

## IX. Insulator to Metal Transitions in BaX, etc.

The first insulator converted to a metal in Ruoff's group in a DAC was *BaTe*.

T.A. Gryzbowski and A.L. Ruoff. Band-Overlap Metallization of *BaTe*. *Phys. Rev. Lett.*, **53**, 489 (1984).

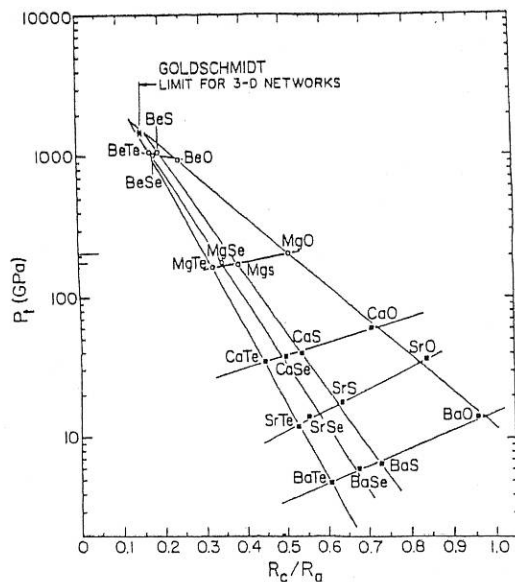
A metal is characterized in part by a low electrical resistivity. *Cu* is a very good metal with  $\rho = 1.6 \times 10^{-8} \Omega$  at 300K while a less robust metal is *Zr* with  $\rho = 43 \times 10^{-8} \Omega - m$ . Somewhat smaller values are permitted. The next necessary condition is that  $\rho$  decreases as the temperature decreases approximately according to  $\frac{1}{T}$  where  $T$  is the absolute temperature. Metals can also be characterized by their refractive index,  $n + ik$ , and by their absorption coefficient. The quantity  $k$  is called the extinction coefficient.

Gryzbowski measured  $\rho$  in the DAC by the 4-lead van der Pauw technique which was first used at high pressure by the Ruoff group. Resistivity studies showed band overlap at  $V/V_0 = 0.65$  and  $P = 20$  GPa and that  $\rho(100K) = \frac{1}{3}\rho(300K)$ . Unfortunately, the diamonds broke on further cooling. Optical studies showed metalization at  $V/V_0 \sim 0.65$ . From X-ray studies they found a phase transition at  $V/V_0 = 0.907$  and  $P = 4.8$  GPa from the *NaCl* ( $B_1$ ) structure to the *CsCl* ( $B_2$ ) structure. *BaSe* and *BaS* show the same transition at 6.0 and 6.4 GPa while *BaO* transforms first to the *NiAs* ( $B_8$ ) structure (also 6-fold coordinated) and then to a near 8-fold tetragonal structure at 15 GPa, first observed by Lin-gun Lui.

S.T. Weir, Y.K. Vohra and A.L. Ruoff. High-Pressure Phase Transitions and the Equation of State of *BaS* and *BaO*. *Phys. Rev. B*, **33**, 4221 (1986).

- *Ruoff's group made careful and complete metallization studies of BaTe, BaSe and BaS in the diamond anvil cell with the introduction four-lead van der Pauw technique into high pressure studies with complementary optical techniques.*

The figure shows the pressure at which phase transitions to 8-fold coordinated structures (closed circles) and the expected pressures for transitions to 8-fold coordinated structures (open circles).



C.H.B. Zhang, Y. Mori, C. Narayana and A.L. Ruoff. *X-ray studies of BeO to 126 GPa. Science and Technology at High Pressure*, ed. by M.H. Manghnani, W. J. Nellis, and M.F. Nicol, Universities Press, Hyderabad, India (2000) p. 518.

In the *Mg* group, it was shown for the first time that the stable phase at  $P = 0$  was the *NiAs* phase (also 6-fold coordinated).

T. Li, H. Lui, R.G. Greene, A.L. Ruoff, S. Trail and F.J. Di Salvo, Jr. High Pressure Phase of *MgTe*: Stable Phase at *STP*? *Phys. Rev. Lett.*, **74**, 5232 (1995).

*MgSe* has a *B1* to *B8* transition at low pressure (1-3 GPa) and persists in the *NiAs* phase to 99 GPa where it begins a prolonged continuous transformation by internal atom motions ending at about 202 GPa to the 7-fold coordinated *B28* structure (also called the iron silicide structure). There was no noticeable volume change from 99 to 202 GPa, a characteristic of second-order phase transitions; theoretical calculations showed a tiny change.

A.L. Ruoff, T. Li, A.C. Ho, M-F. Pai, H. Luo, R. Greene, C., Narayana, J.C. Molstad, S. Trail and F.J. Di Salvo, Jr. *Phys. Rev. Lett.*, **81**, 2723 (1998).

- *This was the first determination of internal atom positions above 100 GPa.* It was shown that the isoelectronic set of *BeTe*, *CsI* and *Xe* follow the Goldhammer and Herzfeld dielectric catastrophe model as do the chalcogenides *BaTe*, *BaSe* and *BaTe*.
- *Ruoff discovered that, for the alkaline chalcogenides, the alkali metals and the rare gas solids (all closed shell systems),  $n^2 E_g(\text{Ryd}) = \pi/2$ , where  $n$  is the refractive index and  $E_g$  is the energy band gap.*

A.L. Ruoff. Empirical Relation Between the Energy Band Gap and the Refractive Index in Closed Shell Systems, *Mat. Res. Soc. Symposium Proc.*, **22**, Part 1, 279 (1984).

Ruoff's group found the alkaline chalcogenides to be a happy hunting grounds, inspired by Pauling, J.C. Phillips, Goldschmidt and Sheraga.

## X. Metalization of Molecular Solids

Following their metalization of  $BaTe$ ,  $BaSe$  and  $BeS$ , Ruoff's group began the hunt that led to the metalization of oxygen (95 GPa) and sulfur (95 GPa) at 300K.

S. Desgreniers, Y.K. Vohra and A.L. Ruoff. Optical Response of Very High Density Solid Oxygen to 132 GPa. *J. Phys. Chem.*, **94**, 1117 (1990).

A.L. Ruoff and S. Desgreniers. *Very High Density Solid Oxygen: Indications of a Metallic State, In Molecular Systems Under High Pressures*, ed. by R. Pucci and G. Piccitto, Elsevier Science. North Holland, **123**, (1991).

H. Luo, S. Desgreniers, Y.K. Vohra and A.L. Ruoff. High Pressure Optical Studies on Sulfur to 121 GPa: Optical Evidence for Metallization. *Phys. Rev. Lett.*, **67**, 2998 (1991).

H. Luo, S. Desgreniers, Y.K. Vohra and A.L. Ruoff. Optical Absorption and Reflection Studies on Sulfur: Evidence for Metallization. *Recent Trends in High Pressure Research*, ed. by A.K. Singh (1991), Oxford and IBH Pub. Co., New Delhi (1992), p. 374.

It should be noted that in order to load these gases into the pressure cell, the piston-cylinder was placed inside a large steel cylinder in which the gas pressure was raised to 0.2 GPa. For the sake of convenience, the small cylinder-piston noted earlier (BABY BERTHA) used was satisfactory for these lower pressure studies but would not suffice to get, say, 600 GPa with current techniques.

• *These elegant experimental results proving the metallization of oxygen and sulfur rigorously passed the test of time.*

Eight years later, Shimizu et al., *Nature*, **390**, 3767 (1998) confirmed the metalization of oxygen and showed that at 93 GPa, oxygen became a superconductor with  $T_c = 0.6K$ .

After the metalization of sulfur by Ruoff's group Prof. Marvin Cohen's group did theoretical calculations and predicted that sulfur would be a superconductor.

The result of both groups was subsequently confirmed six years after the initial metalization by Struzkin et al., *Nature*, **360**, 382 (1997), when they showed that at 95 GPa and 10K, sulfur became a superconductor, and that  $T_c$  increased to 15K as  $P$  increased to 160 GPa, and then jumped to 17K and then  $T_c$  decreased as  $P$  increased. It should be noted that previous X-ray studies on  $S$  to 212 GPa had found a transition to the  $\beta - Po$  structure at 162 GPa.



H. Luo, R.G. Greene and A.L. Ruoff. *B – Po* Phase of Sulfur at 162 GPa: X-ray diffraction studies on *S* to 212 GPa. *Phys. Rev. Lett.*, **71**, 2943 (1993).

Huan Luo won the Jamieson Award given by AIRAPT in 1993 for his studies of sulfur.

Ruoff's group also showed in a cooperative effort that xenon became a transparent conductor at 150 GPa.

R. Reichlin, K.E. Brister, A.K. McMahan, M. Rose, S. Martin, Y.K. Vohra and A.L. Ruoff. Evidence for the Insulator-Metal Transition in Xenon from Optical, X-ray and Band Structure Studies to 170 GPa. *Phys. Rev. Lett.*, **62**, 669 (1989).

This paper was accompanied by a similar success by Silvera's group on xenon published in the same issue (instant confirmation).

## XI. Attempted Metallization of $CsH$

As a result of a discussion between Ruoff and Baranowski about  $CsH$ . Ruoff looked further into  $CsH$ . He noted that Hockheimer et al., (1985) had shown that  $CsH$  has a bulk modulus at 300K of 7.6 GPa while Mao et al., had determined that the room temperature freezing point of hydrogen was 5.4 GPa, and that its bulk modulus there was 15.6 GPa. [For comparison, lithium at 300K has  $B_o = 12$  GPa].

Studies on  $CsH$  led by Ruoff's graduate student, Kouros Ghandehari resulted in three publications involving Ruoff's group and DiSalvo's group.

K. Ghandehari, H. Luo, A.L. Ruoff, S. Trail and F.J. DiSalvo, Jr. New High Pressure Crystal Structure and Equation of State of Cesium Hydride to 253 GPa. *Phys. Rev. Lett.*, **74**, 2264 (1995).

A.L. Ruoff, K. Ghandehari, H. Luo, S. Trail and F.J. DiSalvo, Jr. Phonon Reflectivity Behaviour in  $CsH$  and  $CsD$  at Megabar Pressures: Phonons in the Near  $IR$  ( $\lambda = 1 - 2\mu m$ ). *Solid State Comm.*, **100**, 777 (1996).

K. Ghandehari, H. Luo, A.L. Ruoff, S. Trail and F.J. DiSalvo, Jr. Band Gap and Index of Refraction of  $CsH$  to 251 GPa. *Solid State Comm.*, **95**, 385 (1995).

While highly compliant at  $P = 0$  ( $B_0 \sim 8$  GPa),  $CsH$ , when squeezed to 253 GPa, was found to have  $B(251 \text{ GPa}) = 881$  GPa, over twice the value of diamond at  $P = 0$ . The structure at  $P = 0$  is the  $NaCl(B1)$  type which transforms to the  $CsCl$  type at 37 GPa and then at 17.5 GPa ( $V/V_0 = 0.53$ ) to the orthorhombic  $CrB$  structure (space group  $Cmcm$ ). The  $Cmcm$  space group is predicted to be a product space group of the parent  $CsCl$  structure involving a displacive phase transitions with  $X_5^+$  or  $X^-$  mode softening. Nineteen peaks were indexed with excellent positional fits to the  $CrB$  structure and very good intensity fits. At 253 GPa and 300K  $V/V_0 = 0.26$  and as noted it is extremely stiff elastically. Theoretical studies of  $CsH$  confirmed the crystal structure.

R. Ahiyu, O. Erickson, J.M. Wills and B. Johansson. Theoretical high-pressure studies of caesium hydride. *Journal of Physics: Condensed Matter*, **10**, L153 doc:10.1088/0953-8994.

The energy band gap at 251 GPa was  $1.9eV$  and the refractive index was 3.2 with  $k = 0$ ; hence  $n^2Eg = 19.2eV$ , compared to the expected  $n^2Eg(Ryd) = \pi/2$  or  $n^2Eg(eV) = 21.4$ , by Ruoff's relation noted earlier. This suggests that at 250 GPa  $CsH$  is an ionic solid.

- *CsI showed interesting similarities to H<sub>2</sub>: (1) The energy band gap was 1.9eV at 250 GPa for CsH which is the same as for hydrogen (shown later) at 342 GPa. (2) The calculated volume of solid hydrogen at the freezing point at 300K shows the same factor of four reduction as does CsH at 300K and P = 0 when the pressure is increased to 250 Gpa.*
- *The rising reflectivity in the i - r (second paper) was shown by isotopic-studies to be owing to phonons and not to a rising band edge.*

## XII. Why a Sequence of High Pressure Studies on a Solid Sample is often not a Static High Pressure Experiment

Researchers say “static high pressure measurements” because that may be a good approximation in some cases after a sufficient time is allowed after the pressure is changed.

However, during the pressure change in the DAC, plastic deformation (of both the GASKET and the SOLID SAMPLE) is occurring, most dislocations are moving, and there is a net increase of dislocations and vigorous production of point defects. This leads to greatly enhanced diffusion rates as clearly shown by Balluffi and Ruoff.

R.W. Balluffi and A.L. Ruoff. Enhanced Diffusion in Metals during Plastic Deformation. *Appl. Phys. Lett.*, **1**, 59 (1962).

R.W. Balluffi and A.L. Ruoff. On Strain-Enhanced Diffusion in Metals. I. Point Defect Models. *J. Appl. Phys.*, **34**, 1634 (1963).

A.L. Ruoff and R.W. Balluffi. Strain-Enhanced Diffusion in Metals. II. Dislocation and Grain-Boundary Short-Circuiting Models. *J. Appl. Phys.*, **34**, 1848 (1963).

A.L. Ruoff and R.W. Balluffi. On Strain-Enhanced Diffusion in Metals. III. Interpretation of Recent Experiments. *J. Appl. Phys.*, **34**, 2862 (1963).

A.L. Ruoff. Diffusion During Deformation Measured by Surface Intensity Methods. *J. Appl. Phys.*, **36**, 2207 (1965).

Ruoff had spent his first Sabbatical leave at University of Illinois. It was the year after Ruoff had taught the first dislocation course at Cornell (which inspired Prof. H.D. Block to write the poem “A Crystal Lament.” See

A.L. Ruoff. *Materials Science*, Prentice Hall, Englewood Cliffs, NJ (1973) p. 686.

Diffusion occurs very much faster in grain boundaries and down dislocations (pipe diffusion) than in the bulk. Even if the dislocations are static, they can readily fill with an impurity and with the very high density present in heavily plastically strained materials become colored and blackened by the solute in the dislocations. Now imagine a dislocation filled with impurities. The impurity atoms in the dislocation will slowly diffuse outward into the bulk. However, if stress moves the dislocation during a pressure change, the debris (solute)

remains behind and the dislocation then readily accumulates more solute. The repetition of this process leads to enhanced “bulk” diffusion.

- *Ruoff notes: the process of diffusion enhancement by plastic deformation during pressure changes can wreak havoc in the study of hydrogen, if metal electrodes or gaskets which are nascent hydrogen producers are present.*

Ruoff published a warning about this in his 342 GPa paper on hydrogen in 1998 (to be discussed later).

### XIII. Hydrogen at Ultrapressures is a Voracious Scavenger

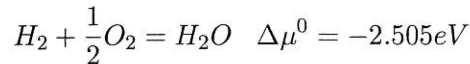
In 1988 Mao et al. published room temperature  $P(V)$  data for  $H_2$  from the freezing pressure (5.4 GPa, where  $V = 8.291\text{cm}^3/\text{mole}$ ) to 26.5 GPa where  $V = 4.791\text{cm}^3/\text{mole}$ . Ruoff computed the chemical potential of  $H_2$  vs. pressure. At  $STP_0 \Delta\mu^0 = 0$  there is good  $P - V$  data available at 300K to the freezing point at 5.4 GPa where  $V_{H_2} = 8.29\text{cm}^3/\text{mole}$ . Loubeyre et al. Nature (1996) obtained the EOS to 109 GPa to 300K. Their Vinet equation was used to calculate the quantities in Table 1.

Table 1: Hydrogen Variables vs. Pressure

$P(\text{GPa})$	$V_{H_2}(\text{cm}^3/\text{mole})$	$\Delta\mu(\text{eV})$	$B(\text{GPa})$
5.4	8.29	0.85	18.5
10	6.70	1.20	32
20	5.28	2.16	60
60	3.50	2.93	140
100	2.92	5.18	250
200	~ 2.08	~ 7.9	~ 480
250	~ 1.88	~ 9.1	~ 590
300	~ 1.74	~ 10.2	~ 720
350	~ 1.60	~ 11.1	~ 760
600	~ 1.23	~ 15.4	~ 1273

Note: the estimated ratio  $V(250)/V(5.4)$  is 3.8 for  $H_2$  and the measured ratio is 3.9 for  $CsH$  discussed in Section XI.

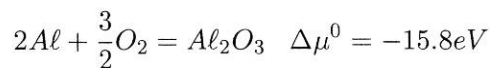
Consider:



These two reactants can be comingled without reaction in a metastable state. A tiny spark causes an explosion.

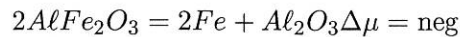
- $H_2$ , at a high pressure is (in a thermodynamic sense) a voracious scavenger.

Another metastable state is aluminum on the wings of airplanes:



A thin layer of coherent oxide on the surface prevents further oxide formation.

However, the famous thermite reaction



used to bring down old, high buildings (straight down) works because the enormous heat given off by the burning of the aluminum melts the steel beams to which the thermite is attached.  $H_2$  as a reactant at high pressure also often causes a similar negative  $\Delta\mu$  for a reaction product.

If, e.g., there is a metal which, perhaps by raising the pressure in the presence of  $H_2$ , has  $\Delta\mu$  become negative, (the reaction  $M + \frac{1}{2}H_2$  has  $\Delta\mu$  negative) it may remain in a metal stable state because the activation energy,  $\Delta\mu^*$ , is too large and the rate of reaction, being proportional to  $e^{-\Delta\mu^*/kT}$  and is too slow. The kinetics need a spark.

This can be accomplished with a catalyst which absorbs  $H_2$  and releases  $H$  atoms. Such nascent hydrogen formers are widely used in the petroleum industry and the chemical industry. They include *Re, Ag, Cu, Au*, etc. For the reaction shown, the activation energy,  $\Delta\mu^*$ , is reduced by  $2.2eV$  and the reaction readily proceeds at 300K.

Inasmuch as "like dissolves like" metal atoms which form hydrides are likely to be soluble in hydrogen. Moreover, because of the presence of dislocations and pipe diffusion and the enhanced diffusion owing to plastic deformation during pressure change, a solution of metal in hydrogen can readily form.

#### XIV. Studying Pure Hydrogen is Difficult Because It Has to be Kept Pure

If nascent hydrogen formers are present in the cell, it is extremely unlikely that the hydrogen itself will remain pure. It is likely that metal hydrides will form, and it is likely that metals will dissolve in the hydrogen.

It is likely that “black hydrogen” will be “observed” but what is being observed is a solution in a hydrogen solvent or suspended MH particles in a solution, not hydrogen.

Ruoff was intrigued by studies on metal hydrides and carefully followed the work of the Ponyatovsky group and the studies of Baranowski and Thacz.

He had highlighted in his notebook in 1984 the following comment:

“To date hydrides of all transition metals have been synthesized except those of the remaining four platinum metals and **TUNGSTEN**.”

V.E. Antonov, I.T. Belash, V. Val Malyshev and E.G. Ponyatovsky. The solubility of Hydrogen in Platinum Metals under Pressure. *Platinum Metals Rev.*, **28**, 158–163 (1984).

This is why Ruoff used costly ultrapure gaskets of *W* which were checked by surface analysis for nascent hydrogen formers by three different analytical laboratories who found none.

Ruoff notes that along with the bulk *W* and the bulk  $H_2$  there is another phase, the interfacial phase and it is entirely possible that an impurity such as *Re* in low concentration in the bulk *W* gasket, may be at a high concentration in the interface, and may even be a monolayer.

Ruoff points to the example in which his son Rodney produced graphene, by use of carbon dissolved in copper, with partitioning on the surface.

● *All data obtained on  $H_2$  at high pressure with nascent hydrogen formers present are likely to be data on solutions and/or MH suspended in solution.*

A.L. Ruoff. “The difficulty of studying pure hydrogen at ultrapressure, in preparation.”



## XV. Faulty Claims of Metallic Hydrogen

Two early claims not using diamond cells faded away because:

1. The necessary pressures could not possibly have been reached. It is doubtful that 100 GPa was reached.
2. The electrical resistance drops observed were most assuredly shorts.

The third claim that  $H_2$  became metallic in the hydrogen cell at 150 GPa based only on reflectivity, ignoring absorption data, was published with great news and excitement and was retracted in a few lines in another paper several years later.

The fourth claim was made in 2011 by Eremets and Troyan who earlier had led the group who claimed to have made superconducting  $SiH_4$  at 50 GPa. The “superconducting  $SiH_4$ ” turned out to be platinum hydride as shown by

O. Degtyareva et al. *Solid State Commun.*, **149**, 1583 (2009).

This fourth claim of making metallic  $H_2$  at 275 GPa at 300K in 2011 did not give a single measured property of a material. There were severe impurity problems and electrical shorts (see Figure 6 of the reference to Poon et al. in Section VIII). Their resistance dependence as a function of temperature is **TOTALLY CONTRARY** to that required of a metal. Their “black hydrogen,” i.e., polluted hydrogen occurred at a substantially lower pressure than observed by other finders of “black hydrogen.” That is a necessary and sufficient condition which disproves metallization. Einstein wrote, “A thousand experiments which agree with my theory do not prove it is right, while one experiment can prove me wrong.” Repeating a technique, proved wrong in one case, is likely to be courting trouble.

## XVI. Two Results Which Showed No Signs of Metallization: one at 290 GPa and one at 342 GPa

Before 2012 there were two published papers on  $H_2$  at 300K which showed no “black hydrogen,” one at 290 GPa and one at 342 GPa. Both used ultrapure  $W$  as gaskets as noted earlier.

In the first Raman measurements were made at 34 pressures to 273 GPa and X-ray pressure measurements were made to 290 GPa and a micrograph was taken which showed only transmitted yellow light through the well-centered round sample but then a fracture occurred. A metal sample would not transmit light.

A.L. Ruoff. *Hydrogen at Multimegabar Pressures in High pressure Science and Technology*. Ed. by W. Trzeciakowski, World Scientific. Singapore (1996), p. 25

The second experiment showed no black sample but showed yellow (nearer to orange) light transmitted and a Raman peak at 342 GPa. The band gap is near  $1.9eV$ .

C. Narayana, H. Luo, J. Orloff and A.L. Ruoff. Solid Hydrogen at 342 GPa: No Evidence for a Alkali Metal. *Letters to Nature*, 393, 46 (1998).

Ruoff notes that tungsten hydride has since been produced by others, occurring in the presence of free  $H$  atoms.

It was first produced by Indian scientists using a **rhenum** gasket with powdered  $W$  in the sample hole with  $H_2$ . It was then produced by Akahama et al., in the same way.

It was next produced by Strobel et al. using a  $W$  gasket from a mixture of  $SiH_4$  and/or  $H_2$  plus  $(SiH_4)(H_2)_2$  probably with some decomposition at modest pressures producing  $SiH_{4-m}$  and  $mH$ .

Recently M. Hanfland, J.E. Proctor, C.I. Guillaume, O. Degtareva and E. Gregoryanz wrote: “High Pressure studies on silane ( $SiH_4$ ) revealed that it does not metallize at 50 GPa, but instead goes through a pressure induced amorphization above 60 GPa recrystallizing into a polymeric phase at around 90 GPa. Silane remains insulating up to at least 130 GPa.”

- *The conclusion of Ruoff’s group:  $H_2$  is still a large band gap semiconductor with a gap of about  $1.9eV$  at 342 GPa.*

Addendum: Another study (14 years later) by Zha et al., PRL, 2012 confirms this conclusion to 360 GPa.