

# ENGINEERING

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## **Arthur Ruoff in Engineering: Cornell Quarterly**

MEGABAR PRESSURES IN SUBMICRON VOLUMES

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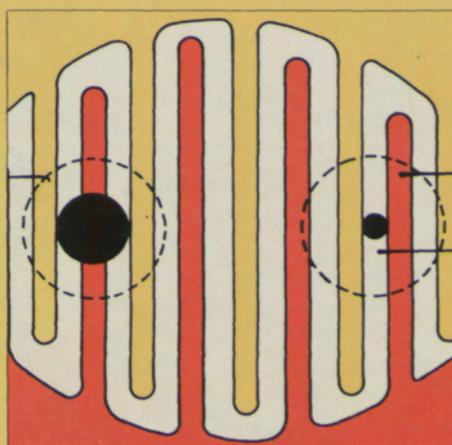
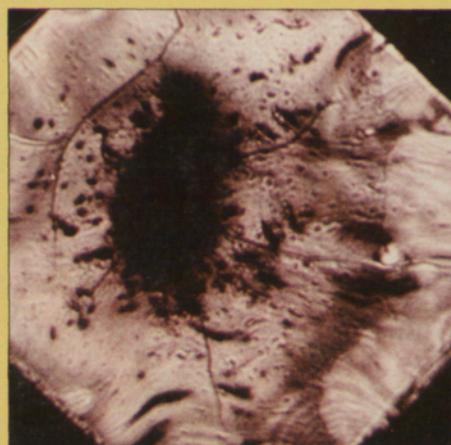
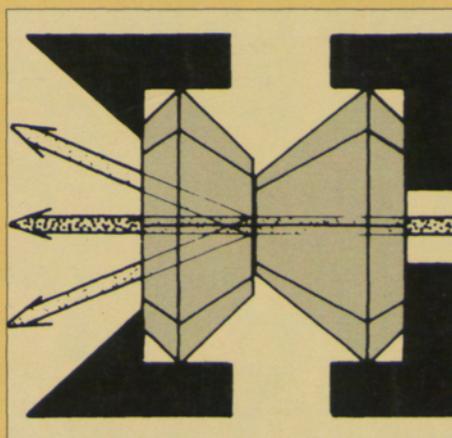
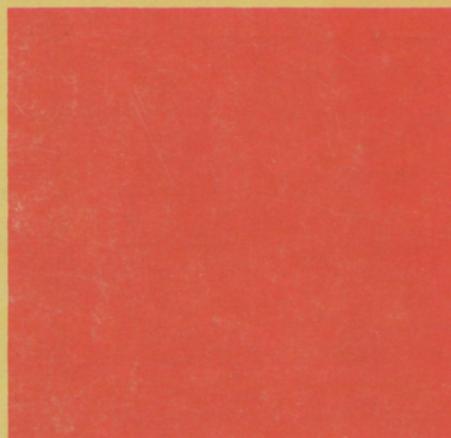
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# ENGINEERING

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**MATERIALS  
AT ULTRAHIGH  
PRESSURES**

# MEGABAR PRESSURES IN SUBMICRON VOLUMES

*by Arthur L. Ruoff*

The pressure in an ordinary automobile tire is about 3 bars, approximately three times atmospheric pressure. City water pressure may be 4 to 5 bars. The pressure at the deepest spot in the ocean is about 1,000 bars or 1 kilobar (kbar). Many commercial processes are carried on at pressures of 1 to 5 kbars; diamonds are synthesized at about 50 kbars. The pressure at the center of the Earth is about 3.7 million bars or megabars (Mbars). It is at pressures in the megabar range that the work of my research group is focused.

Under these extreme pressures, materials have properties very different from those they exhibit under ordinary conditions. If the material is a liquid, there can be an enormous increase in viscosity and a drastic change in the freezing point. A solid sometimes assumes a new, more condensed structure. New chemical compounds may form, or existing compounds may break up into their elements. Nonconductors become metals, and often these new metals are superconductors at low temperatures.

The industrial potential of this modern-day alchemy is enormous. For

example, if pressure-induced superconductors prove to be metastable—if they can be kept in metallic form after the pressure is released—they could be used in many electrical and electronic applications. But current research is directed primarily to basic scientific studies and to the development of necessary techniques. Significant progress has been made in attaining ultrahigh pressures and in producing and examining new forms of materials. Our group at Cornell has had some exciting successes: we have made metallic xenon, for example, and we have converted sulfur, one of the best electrical insulators, to a metal. A new approach is to make use of unique new submicron fabrication and x-ray facilities at Cornell to create and examine materials in new forms.

## HIGH-PRESSURE EFFECTS ON PHASE AND STRUCTURE

What happens to materials as a result of pressure? Essentially, the atoms are pushed closer together, drastically altering the macroscopic properties as well as the molecular structure.

The magnitude of viscosity change, for example, is difficult to conceive. A mixture of three parts methanol and one part ethanol increases in viscosity by a factor of 10 trillion ( $10^{13}$ ) when a pressure of 100 kbars is applied. Under pressure, materials freeze at higher temperatures than they do under atmospheric conditions. Liquid hydrogen, for instance, freezes at 16°K at atmospheric pressure, but at 56 kbars, the freezing point is 300°K, about room temperature. A solid may change to a new structural form with a higher coordination number (the number of nearest-neighbor atoms or ions). In sodium chloride, for example, each sodium ion has six chlorine ions surrounding it at atmospheric pressure, but above a few hundred kbars each sodium is surrounded by eight chlorines. Materials scientists say that the compound has undergone a phase transformation from the sodium-chloride-type structure to the cesium-chloride-type structure.

The transformation of graphite to diamond is another example of a pressure-induced increase in coordina-

*“The industrial potential  
of this modern-day alchemy  
is enormous.”*

tion number. In graphite, which is the equilibrium structure of carbon at atmospheric pressure, each atom has three nearest neighbors. Above about 14 kbars at room temperature, diamond is the equilibrium structure, and each carbon has four nearest neighbors. This may seem puzzling, for we know that both graphite and diamond exist at atmospheric pressure. The explanation is that diamond is metastable under ordinary conditions. A thermodynamicist would say that graphite has a lower free energy than diamond at room temperature and pressure; the carbon atoms in diamond would “like” to arrange themselves into the graphite structure and thereby lower their free energy. The rate of this rearrangement is slow, however: one need not worry about a diamond gem reverting to graphite. But if the temperature were raised substantially, say to 1,700°C, this reversion would occur rapidly.

The transformation of graphite to diamond at high pressure is the basis of a large industry: synthetic diamond production. In fact, most industrial

ally. They are used for such diverse operations as grinding hard materials such as the turbine blades in a jet engine, cutting grooves in highways, scratching designs on Steuben glass, slicing silicon crystals into wafers, and drilling oil wells. In the United States, the General Electric Company has a major synthetic diamond plant in Columbus, Ohio. There are other synthetic diamond plants in France, Ireland, Japan, Russia, South Africa, and Sweden.

Silicon, both as an element and in compounds, also undergoes an increase in coordination number under high pressure. Normally silicon exists in silicate structures, as part of the  $(\text{SiO}_4)^{4-}$  radical and has four nearest-neighbor oxygen atoms, but at a few hundred kbars, six-fold coordination occurs; this process is of enormous importance in geology. Elemental silicon shows an increase in coordination number from four to approximately eight at about 120 kbars; in the process, it changes from a semiconductor to a metal. Diamond, which has the same crystal structure as silicon, will probably transform to a metal at about 2 Mbars.

#### COMPOUND FORMATION AND DECOMPOSITION

Not only changes in crystalline structure, but also the formation of crystalline compounds can be accomplished under high pressure. Cubic boron nitride, for example, is a metastable material commercially made by a process similar to that used for diamond: ordinary BN is dissolved in liquid metal, pressure-treated, and then precipitated as the cubic form. But research now underway is showing how the cubic form can be produced at much lower pressures and in larger quantities by growing it from a solution containing boron and nitrogen compounds.

The opposite process—the decomposition of a compound into its elements—can also occur under high pressure. This happens with  $\text{C}_3\text{S}_2$ , a compound we have worked with in our laboratory. Our hope was that the carbon produced at high pressure and room temperature would be in the form of diamond. It wasn't; but had this process worked, we might have synthesized diamond at 15 kbars instead of the 50 kbars used in commercial practice.

A variation of decomposition under pressure is a reaction in which the original compound forms a different compound plus an element. Recently there has been much excitement about results suggesting that cuprous chloride exhibits unusual magnetic behavior (characteristic of superconductors) when it is subjected to high pressures. There is some evidence that the reaction taking place is  $2\text{CuCl} \rightarrow \text{CuCl}_2 + \text{Cu}$ .

#### TRANSFORMING INSULATORS INTO CONDUCTING METALS

At sufficiently high pressures, all semiconductors and insulators are expected to be metals (pure semiconductors at low enough temperatures are also insulators). For example, zinc sulfide, an excellent insulator, becomes metallic at about 150 kbars. The semiconducting III-V compound gallium phosphide becomes metallic at about 200 kbars. Mike Chan, a graduate student in my group, is looking at aluminum nitride; there is a theoretical prediction that it will transform to a metallic phase at 0.9 Mbar. An indication of the relative pressures needed for metallic transformation is given by the position of the elements in the periodic chart (see Table I).

In our laboratory at Cornell, we have conducted high-pressure experiments with several of these nonmetallic elements. We have cooled iodine metal (at pressure) to 1°K with no sign of superconductivity. Currently Millard Baublitz, a student in my group, is attempting to study it at temperatures down to 0.3°K, but perhaps even that will not be low enough to produce superconductivity. In other work, we showed that sulfur, which is ordinarily an extremely good insulator, becomes

Table I  
METALLIZATION OF NONMETALLIC ELEMENTS

Groups					
IIIb	IVb	Vb	Vlb	VIIb	VIII
				H	He
B	C	N	O	F	Ne
	Si	P	S	Cl	Ar
	Ge	As	Se	Br	Kr
			Te	I	Xe
					Rn

There are two general rules about the pressure needed to transform the nonmetallic elements to metallic conductors: (1) in a given row of the periodic table, the required pressure increases from left to right; and (2) in a given column the transition pressure increases from bottom to top. Thus helium will require the most pressure. None of the first- or second-row elements have been made metallic; boron should transform at a modest pressure of a few hundred kbars, although the kinetics of the transition may make high temperatures necessary. The elements Si, Ge, P, As, Se, Te, and I all become metallic below 200 kbars, and all of these metals except iodine have been found to be superconductors at high pressure.

metallic at room temperature at 300 kbars. And we found that solid xenon became metallic when pressurized to 320 kbars at 32°K. (Of the inert gas solids, radon should transform at the lowest pressure, but because it is radioactive, we chose not to work with it.)

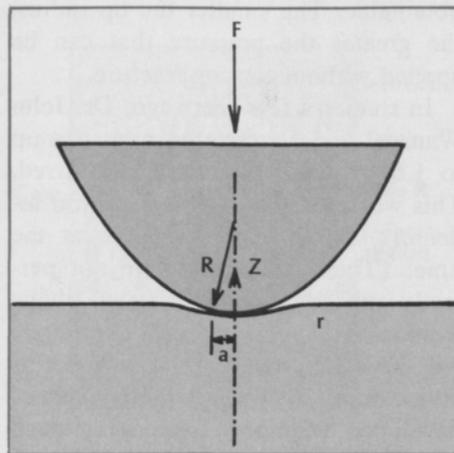
We think that oxygen and hydrogen are exciting possibilities for future research. A metal transition in oxygen should require a pressure of about 1 Mbar. For hydrogen, a pressure variously estimated at 1.6 to 7 Mbars might be needed.

#### ATTAINING HIGH PRESSURES IN THE LABORATORY

There are two general rules for obtaining high pressures: (1) use the hardest substance known for the apparatus; and (2) create the pressure in the smallest volume possible. These criteria determine our laboratory technique.

Diamond is the stiffest and hardest material on Earth, with the highest yield strength. It has the same crystal-line structure as silicon and germanium,

Figure 1



but is about ten times stiffer and stronger. All three of these materials are brittle—tiny scratches on their surfaces will greatly decrease their fracture strength—and all three plastically deform if fracture is prevented. The bulk compressive strength of diamond is about 350 kbars, which is very high; the next strongest common material, sintered tungsten carbide, has a yield strength of 52 kbars (as determined by Prakash Panda, a graduate student, and me), and ultra-strength steels have yield strengths in the region of only 20 kbars. Anvils made of diamond would begin to yield at 500 kbars and could sustain a maximum pressure, when heavily deformed, of about 1 Mbar.

If truly perfect diamonds were available, much higher pressures could be attained. It has been predicted that the yield strength of perfect diamond would be 4.1 Mbars. But single crystals of diamond, regardless of their sparkle and clarity, are neither pure carbon nor perfect crystals; they contain about 1 percent of impurities, either in solution or as tiny precipitates, and they exhibit crystalline irregularities amounting to about  $10^5$  centimeters of dislocation line per cubic centimeter of material. (Dislocations are significant because plastic deformation occurs by motion of these line defects.) Large dislocation-free crystals of silicon can be grown, and it is not inconceivable that this could be accomplished with diamond. But at the present time, the best alternative is to use a diamond of very small size; if small enough, it will be free of dislocations. Such a region must be about 10 microns ( $\mu\text{m}$ ) in each dimension ( $1 \mu\text{m} = 10^{-6}\text{m} = 10^{-4}\text{cm}$ ).

Accordingly, the technique we use to obtain very high pressures is to press

Figure 1. A schematic of the spherical indenter-flat anvil pressure-generating system. A force  $F$  is applied on the indenter, which has a spherical tip of radius  $R$ . Pressure is exerted over a contact area of radius  $a$ , with a maximum value at the center. The smaller the tip, the larger the pressure attained: with tip radii in the micron range, megabar pressures can be achieved at the center.

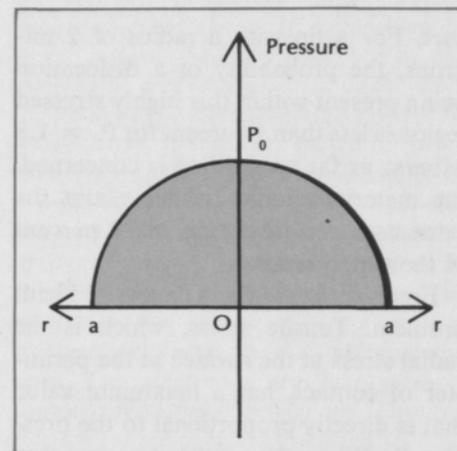
Figure 2. The pressure distribution of the system shown in Figure 1. The maximum pressure,  $P_0$ , is produced at the center of the area of contact, where  $r=0$  and  $z=0$ . The area of contact has a radius  $a$ .

a tiny diamond with a spherical tip—the indenter—against a flat diamond, as shown in Figure 1. This results in a contact pressure distribution, as shown in Figure 2, with a maximum,  $P_0$ , that can be calculated from elasticity theory. The equation we use was formulated by Hertz:

$$P_0 = (3/2)^{1/3} \pi^{-1} (E/1-\nu)^{2/3} R^{-2/3} F^{1/3}$$

where  $E$  is Young's modulus,  $\nu$  is Poisson's ratio,  $R$  is the initial tip radius, and  $F$  is the applied force. This shows that the maximum pressure,  $P_0$ , is pro-

Figure 2



portional to the applied force and inversely proportional to the radius of the indenter tip.

To understand the eventual failure of the diamond, we must consider the shear stress, which causes yielding by dislocation motion, and also the tensile stress, which causes fracture.

The shear stress is a maximum along the axis of revolution at a distance of about  $a/2$  from the contact point (see Figure 2), and falls to about a quarter of this value on a spherical surface of radius  $a$  centered at the point of con-

tact. For a tip with a radius of 2 microns, the probability of a dislocation being present within this highly stressed region is less than 1 percent for  $P_0 = 1.8$  Mbars: as far as yielding is concerned, the material should behave about the same as a perfect crystal in 99 percent of the experiments.

Fracture presents a more difficult problem. Tensile stress, which is the radial stress at the surface at the perimeter of contact, has a maximum value that is directly proportional to the pressure  $P_0$ . When the tensile stress reaches a certain critical value—the fracture strength—a ring crack forms. (The actual shape of the ring crack is determined by the way in which the cleavage planes intersect the surface.) This limits the maximum value of  $P_0$ . Happily, there is an important size effect that helps out, however. It was discovered by Auerbach in 1890 that when a steel bearing is pressed against glass, the fracture strength of the glass increases as the tip radius decreases; we have found that this law applies to diamond over a wide range of tip radii, from 2,000 microns down to the smallest

obtainable. The smaller the tip radius, the greater the pressure that can be applied without causing fracture.

In studies a few years ago, Dr. John Wanagel and I registered pressures up to 1.6 Mbars before failure occurred. This work was done with 2-micron indentors, the smallest available at the time. (These indentors were not perfectly spherical; if their actual shape were taken into account, the pressure we achieved would be calculated as larger than 1.6 Mbars.) We have since developed techniques for making much better tips, with radii as small as a tenth of a micron. Dr. Dan Golopentia and I hope to report soon on the results of tests on these tips, which provide a means of checking theoretical predictions.

#### WORKING WITH SAMPLES IN THE DIAMOND CELL

A sample of material we wish to study under high pressure must be introduced as a very thin film between the flat diamond anvil and the indenter. If the film is sufficiently thin, the pressure distribution will still be given by our basic equation relating maximum pressure,  $P_0$ , to tip radius and applied force. The film may be introduced by vapor deposition, by sputtering, or by evaporation from solution. Very thin samples can also be prepared by thinning a bulk sample by grinding, polishing, and etching.

The pressure attained in an experiment is calculated directly from the Hertz equation. Since this expression includes a constant elastic modulus ( $E$ ), it depends on the assumption of linear elastic behavior of diamond, an assumption that has been justified experimentally. The reliability of the pressure calculation has been verified up to 0.5

Mbar by a direct measurement using Newton's rings (an interference technique), and is considered applicable to about 2 Mbars. Other proved methods of determining high pressure also depend upon the assumption of linear behavior; for example, a measurement based on a shift in the ruby fluorescence peak (see the article in this issue by William Bassett) assumes a linear relation to pressure, and the method is known to be accurate at least to pressures of 100 Kbars.

Since one of the effects of high pressure in which we are most interested is the transition from nonconductor to metal, we must be able to measure changes in electrical resistance. We have developed two techniques to achieve this. By either method, the measurements are taken in a tiny area at the center of the sample, where pressure is near maximum. We call one technique the coated metal film method, and the other the interdigitated electrode method.

In the coated film method, thin films of metal are sputtered onto the highly polished diamond anvil and the diamond indenter, and leads are attached to each. The sample is placed on top of the metal film on the anvil, and the indenter is pressed against the sample. If the sample undergoes a transition to metal, this occurs in the region of highest pressure, along the axis of the indenter, so that resistance measurements pertain primarily to the first material to transform. This method has been used successfully in our laboratory, but it has one shortcoming: if the indenter were to punch through the specimen, a short would occur, and this would be difficult, as a rule, to distinguish from a transition. To avoid

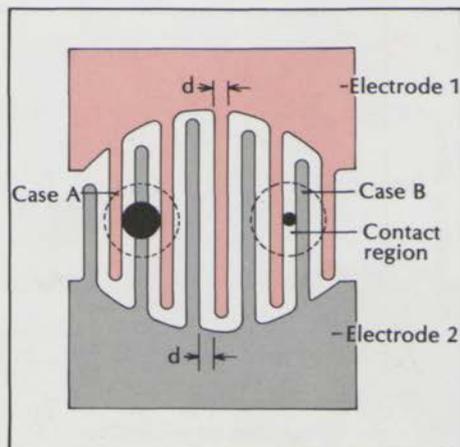
this problem, we invented the second method.

The interdigitated electrode system is diagrammed in Figure 3. This technique, which was developed by Kam-Shui Chan and me, not only prevents electrical shorting, but also eliminates the difficult problem of positioning the indenter precisely so that the tip makes contact between the electrodes. (This is necessary to ensure that the electrodes measure the point of highest pressure, where the transition to metal occurs first.) With the interdigitated system, the indenter tip can be positioned anywhere in the electrode area, since the electrodes are fabricated as grids of seventy-five or more electrode fingers.

Of course, the use of very small tips—needed, as explained, to permit the attainment of very high pressures—requires comparably small electrodes. The grids we use are produced by photolithography in Cornell's new National Research and Resource Facility for Submicron Structures (see the April 1978 issue of this magazine). The width of each finger ( $d$  in Figure 3) was 6 microns in the first experiments we carried out. In the work on xenon,  $d$  was 3 microns, and we are working to reduce the spacing to 0.6 micron using projection lithography. We are also beginning to work with electron beam lithography, which is capable of producing an even finer pattern, and we hope later this year to be able routinely to make electrodes with a width of 0.1 micron.

The electrodes that we have used so far are nickel and are 350 Angstroms thick; in the future, other materials will be used for electrodes for different applications.

Figure 3



Once the electrodes are in place, electrical leads are attached to the anvil base. Then the sample is deposited on the anvil. Finally, the indenter is pressed against the sample-electrode-anvil assembly, and contact is established over the region shown by the dashed circle in Figure 3. When the insulator-to-metal transition pressure of the sample is reached, the newly formed metal closes the circuit. The metallic region is represented in the figure by two solid circles, representing two extremes of possible indenter location. The center pressure will be different for these two cases; but if the finger widths and spacings are very small, the pressure at which the transition is observed will approach  $P_0$ .

#### EXPERIMENTAL RESULTS WITH OUR APPARATUS

Our diamond indenter-diamond anvil system has enabled us to make some interesting studies of what happens to various materials under extreme pressure.

One of the substances we investigated is aluminum oxide, of interest because

*Figure 3. The nonshorting interdigitated electrode system for resistance measurements in very small areas. This assembly is placed on the diamond anvil and covered with a film of nonconducting sample, and then the indenter tip is pressed against it from above. If a transition to metal occurs, the maximum size of the conducting area is determined by the spacing between the electrode fingers and their width ( $d$ ); such areas are indicated in the sketch by black circles corresponding to two possible indenter positions. Finger diameters can be made as small as a fraction of a micron. This system, developed in Professor Ruoff's laboratory, offers the advantage that the indenter can be positioned anywhere in the interdigitated area. The electrodes are fabricated in Cornell's National Research and Resource Facility for Submicron Structures.*

early work at the Moscow High Pressure Institute had indicated a metallic transition at 0.4 Mbar. We did not observe a transition to a conducting phase, however, at pressures up to 1.2 Mbars. It should be noted that an electrical short would give the appearance of an insulator-to-metal transformation. Had we observed a sharp resistance drop, we would have used our nonshorting interdigitated-electrode method to confirm that a transition had actually taken place. The results we obtained demonstrate the necessity of ensuring against

Figure 4

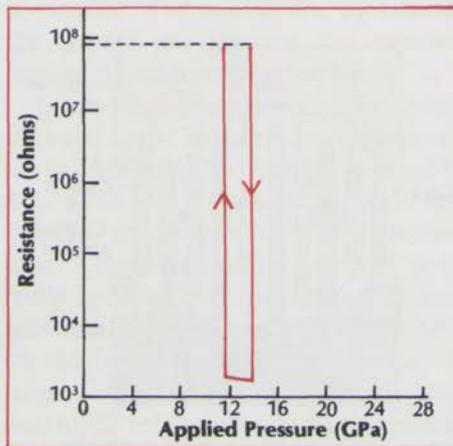


Figure 5

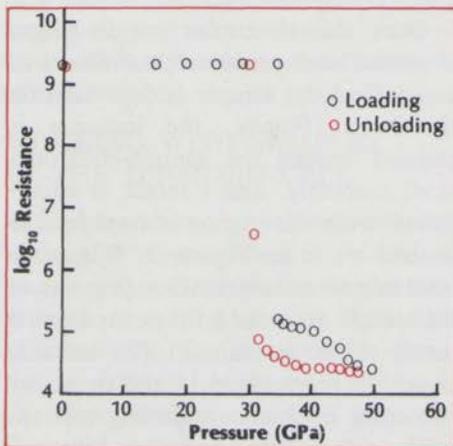


Figure 4. Representative experimental results for the determination of the pressure at which zinc sulfide transforms to a metal. The transition is detected in the diamond-anvil cell as a drop in resistance. These experiments established that the transition occurred at an applied pressure of  $14.0 \pm 0.5$  GPa (1 GPa = 10 kbars); a value of  $15.0 \pm 0.5$  GPa has been obtained on the ruby scale. A control experiment, in which no sample was present, showed no resistance drop.

Figure 5. Experimental results showing the creation of metallic xenon. Transitions from insulator to conductor were observed as drops in resistance (as measured on a Keithley 160B multimeter). The temperature was  $32^\circ\text{K}$  and the interdigitated electrode system was used in the measurements. The readings show a drop in resistance by a factor of  $10^4$  to  $10^5$ , occurring at about 33 GPa (or 330 kbars). This work was done by David A. Nelson, Jr.

electrical shorting in high-pressure resistance measurements.

Using our interdigitated electrode technique, we detected a metallic transition with zinc sulfide (see Figure 4). This was the first observation of the transition in which pressures were measured by a primary method.

Our work with sulfur, in which we produced a transition to metal, revealed another interesting property: resistance was found to drop continuously as the pressure increased, rather than sharply as in most experiments. It appears that

in sulfur the band gaps, and therefore the metallic behavior, vary linearly with pressure. This summer we plan to look for superconductivity in sulfur. Recent reports in the literature suggest that peculiar effects are involved and we are anticipating experiments of great interest.

For our research with xenon, we developed special techniques for handling gaseous samples. We introduced the gas into an evacuated chamber containing the anvil, and cooled it by means of liquid helium flowing through a sup-

porting plate. The thickness of the xenon film condensed on the anvil was measured by a quartz thickness monitor, which uses quartz crystals on the cold plate—one crystal adjacent to the diamond anvil and the other in a permanently evacuated chamber. Results for a representative experiment, showing the transition from insulator to conductor, are given in Figure 5.

We have also studied the electrical behavior of ice at  $78^\circ\text{K}$  in the same apparatus with the same electrodes and indentors. We found that ice remains an insulator to 0.72 Mbar, the highest pressure used.

#### EXPERIMENTS UNDERWAY AND PLANNED

Current and future work will further improve the experimental techniques and equipment, and explore the high-pressure properties of additional materials.

We are continuing to develop tinier tips in order to achieve higher pressures; the ultimate static pressure attainable by use of diamonds will be known soon. Tinier tips will require smaller electrodes, and fabrication techniques for electrodes will also be refined. Three students will be working on these problems.

A special cell that can be used at temperatures as low as  $2^\circ\text{K}$  and with loads as small as 10 grams has been completed and is now being tested. Provided that the diamonds do not fail, this cell should produce a pressure of 2.4 Mbars with a load of 22 grams and a 1-micron indenter tip.

We also have an interesting piece of work in progress which uses a kind of diamond cell developed at the National Bureau of Standards. Here we are using



*A new diamond indenter-anvil system in Professor Ruoff's laboratory will be used at temperatures as low as 2°K. Researchers involved in the experiments include (left to right) Robert Terry, high-pressure technician; Dan Golopentia, senior post-doctoral associate; and Volker Arnold, high-pressure technician. The diamonds and the load cell for measuring the force are in the cylinder just above the bench top.*

We are also beginning to examine the effects of high pressure on the conductivity of a polymer, polyacetylene. This material, which has fibrils containing one-dimensional chains, conducts electricity much better along the chains than perpendicular to them (it has a band gap of about 1.4 eV and can be doped to be a p-type or an n-type semiconductor), and high-pressure studies may elucidate the conductivity mechanism. Perhaps we will convert this semiconducting polymer into a metal; conceivably, however, high pressure will decompose it.

#### LOOKING AHEAD TO HIGH-PRESSURE POSSIBILITIES

Since high pressure drastically alters the characteristics of materials, it raises hopes that radical new technologies may become available. For example, superconductivity effects that occur at high pressures look attractive as transmission costs increase. An idea that is particularly enticing to many people is the formation of metallic hydrogen, which could be used for rocket fuel or as pellets for energy production in fu-

an x-ray technique called Energy Dispersive X-ray Diffraction to study the crystal structure of the new phases produced. This technique has been used in earlier work at Cornell to look at the high-pressure structure of silicon, and is currently being used to study the high-pressure phase of gallium arsenide. With the high-energy x-ray source now available, experiments take a week or more to perform, but we hope soon to be able to use x rays of much higher energy from the Cornell High Energy Synchrotron Source (CHESS) when

construction of this facility has been completed. The shorter time required to gather data—perhaps minutes instead of weeks—will enable us to study the kinetics of transformations occurring at high pressure.

Of the materials we hope to study, oxygen and hydrogen have high priority. We will also continue our studies of metallic iodine, sulfur, and xenon, to see whether we can detect superconductivity. Other materials of considerable interest are methane, ammonia, nitrogen, and, of course, diamond itself.

sion reactors. NASA (which is supporting much of the high-pressure research we are conducting at Cornell) is interested in this possibility.

I am often asked whether I believe that metallic hydrogen will be metastable—that is, whether it will persist at ordinary pressures if kept at low temperatures. My answer is and has been: No. My reason is that the metallic state involves long-range forces, and the only examples of metastability involving large energy differences (0.1 eV per atom, say) involve short-range covalent bonds. Moreover, the degree of “unhappiness” of metallic hydrogen—expressed as a free energy of 4 eV per atom at zero pressure—constitutes a tremendous driving force to return to the molecular state. I could be wrong, but I’ll be very surprised if I am. I am also asked whether I think hydrogen will be a superconductor at relatively high temperatures (above 100°K and possibly at room temperature), as some theorists have predicted. Again, I have to say no. Here my reason is that the theorists have calculated the electron behavior of hydrogen metal on the as-

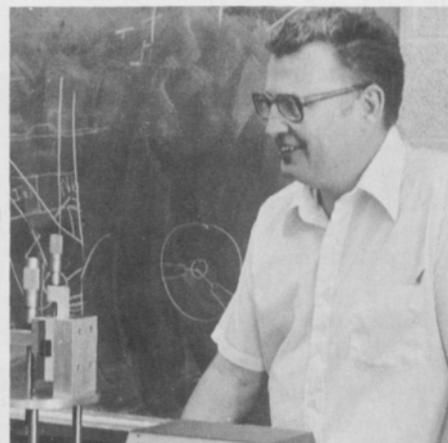
sumption of a static lattice; but in hydrogen the ions (protons) are very light and have appreciable kinetic energy. I expect that accounting for this properly will drastically alter the theoretical predictions.

If I were asked to suggest what will be the highest transition temperature of an element to a metal, I would say that it may be as high as 30°K at pressures of a couple of megabars, and that the metal will be carbon, nitrogen, or oxygen.

Much is still unexplored and unknown in the realm of ultrahigh pressure. There is a long way to go from millions of atmospheres of pressure exerted over dimensions of less than a millionth of a meter to ultrahigh pressures of practical use. But this is partly what makes high-pressure studies an exciting field of research: the possibilities for innovative work are great, and the potential for discovery and application is enormous. Remarkable results are anticipated, hoped for—or perhaps still unimagined.

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*Professor Arthur L. Ruoff is the director of the Department of Materials Science and Engineering and is the Class of 1912 Professor of Engineering. He is known especially for his research in high-pressure phenomena: in his ongoing effort to produce metallic hydrogen, he has developed techniques of applying pressures as high as 1.4 million atmospheres. Ruoff's recent success in producing metallic xenon was announced by the National Aeronautics and Space Administration as an important*



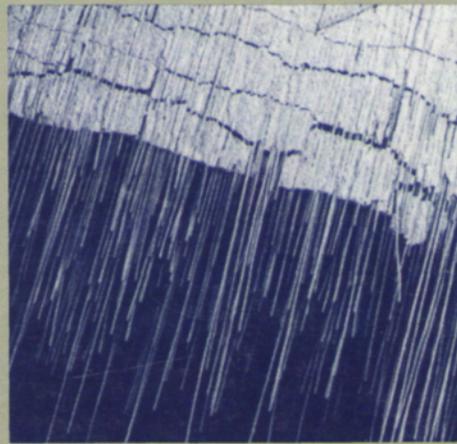
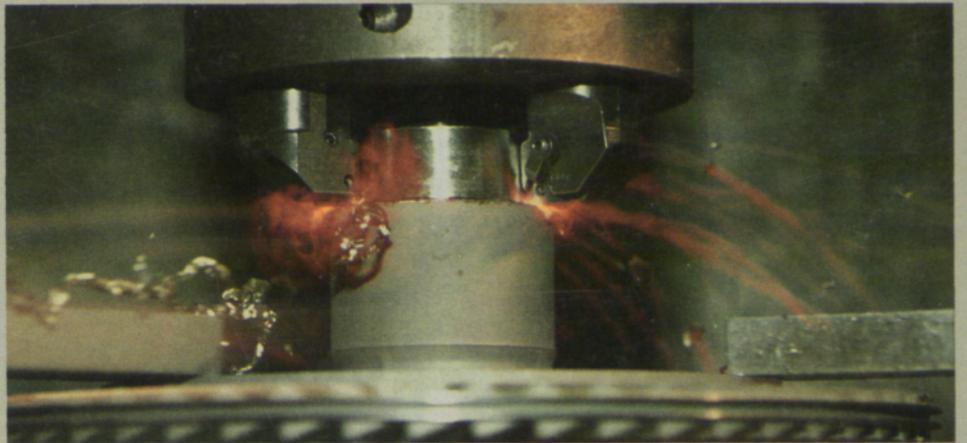
*step toward the goal of producing metallic hydrogen.*

*Ruoff joined the faculty here in 1955 after earning the B.S. degree at Purdue University and the Ph.D. in physical chemistry at the University of Utah. At Cornell he has served as graduate faculty representative for materials science and engineering, and he is a member of the graduate Fields of Applied Physics and Geological Sciences. He has twice served on the executive committee of the University's Materials Science Center, and currently is active in the National Research and Resource Facility for Submicron Structures, both as a researcher and as a member of the program committee. Outside the University he serves as a consultant to numerous industries and laboratories on high-pressure phenomena, and to several universities on techniques of multi-media instruction, a teaching method he has developed in classes here.*

*His honors include a National Science Foundation Senior Science Faculty Fellowship, and the 1967 Western Electric Fund Award, presented by the American Society for Engineering Education for excellence as an educator. He is a fellow of the American Physical Society and has been named Engineer of Distinction by the Engineers Joint Council.*

# ENGINEERING

CORNELL QUARTERLY



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A NEW ERA  
OF CERAMIC  
MATERIALS

# THE CORNELL CERAMICS PROGRAM

*by Arthur L. Ruoff*

The time preceding the seventh millennium is known as the preceramics age, a designation that acknowledges the vital role of ceramics in the development of human society. Pottery, which made possible the storage of agricultural products, was introduced along with agriculture itself; clay tablets were the first durable historical and commercial documents.

Archaeological discoveries, including pottery and tablets, provide clues to history and reveal links to our past. For instance, we know that the cities of Mycenae and Troy in Homer's epic poems truly existed. The island to which Odysseus returned must also have been a real place, probably visited by Homer; perhaps it is the Greek island of Ithaki, after which our upstate New York city of Ithaca is named.

Today we no longer rely on clay tablets, but we do use a great many ceramic materials. We take for granted such common modern artifacts as brick buildings, concrete highways, window glass, ceramic flower pots, and bathroom fixtures. If reminded, we recall that ceramics are a vital component of the sparkplugs in our automobiles and the insulators that hold high-voltage transmission lines. Perhaps

we recall that ceramics line the furnaces in which iron is melted to produce cast iron and steel. Indeed, ceramics made possible first railroads, and then the automobile and trucking industries.

## CERAMICS—FROM CLAY POTS TO SUPERCONDUCTORS

The first ceramic objects were molded from clay and simply dried in the sun. Then it was learned that heating in a fire could make them rock-hard. Over the millennia, both materials and techniques have expanded to the point that definitions are difficult.

What are ceramics? Sometimes it seems easier to say what they are not: they are those solid materials that are not metals and are not based on organic compounds. If forced to be more specific, one could begin by saying that ceramics include oxides (such as aluminum oxide), nitrides (such as silicon nitride), and carbides (such as boron carbide). Sometimes a definition includes nonmetallic inorganic substances in general, and even diamond might be considered a ceramic. Often the term is reserved for materials that can withstand very high temperature.

Ceramics include crystalline materials (such as quartz, one of several crystalline forms of silicon dioxide) and amorphous or glassy substances (such as the material obtained when molten silicon dioxide is cooled rapidly). More often than not, ceramics are impure materials—solid solutions and mixtures of several components. Unlike archaeologists, materials scientists would include in their definition a number of geological materials, mostly oxides. To the materials scientist, marble and granite are ceramics, and so are gemstones such as ruby (which is aluminum oxide,  $\text{Al}_2\text{O}_3$ , contaminated with chromium) and sapphire (which is  $\text{Al}_2\text{O}_3$  contaminated with iron).

In 1987 still another kind of ceramic—complex oxides prepared in the laboratory—made a stir in the scientific world and the news media. The furor began in earnest with the announcement by Paul Chu, a professor of physics at the University of Houston, that he and his colleagues had made a ceramic compound, copper barium yttrium oxide, that was a superconductor at  $96^\circ\text{K}$ , approximately four times the temperature at which metals become superconducting.

*“Today the uses and potential uses of ceramics boggle the imagination.”*

#### THE USEFUL PROPERTIES OF SYNTHETIC CERAMICS

Over the centuries, man-made ceramics have been useful because of their physical properties (animals and insects could not penetrate clay storage vessels, for example), their chemical resistance (the clay pots of Jarmo in Kurdistan have persisted for some nine thousand years), their high melting point (crucial for the lining of steel furnaces), their transparency (valuable for glass objects), and, surely, their low cost.

Today the uses and potential uses of ceramics boggle the imagination. They include:

- *Applications in communications.* The optical fiber, which is revolutionizing the communication industry, is an example of a high-tech ceramic material whose development is an almost unbelievable achievement of materials science and engineering.

Also important are ceramic magnetic materials that are electrical insulators. These are ideal for transformers, such as those in television sets, that are used at high frequencies. (The reason these ceramic materials are good for this application is that they do not exhibit eddy-current heat-

ing, a problem with conducting materials such as magnetic iron.)

- *Applications based on piezoelectric effects.* When placed in vibration by the application of an alternating electric field, piezoelectric ceramic materials can create sound waves (sonar). Conversely, a sound wave can be detected by the electrical pulse it creates when it hits and hence slightly deforms a material such as barium titanate.

- *The fabrication of heat engines.* Unlike metals, ceramics have very high melting points and so retain their strength at the high temperatures at which heat engines are more efficient. Actually, ceramics are already used as part of the electronic controls of automobile engines, as sensors of oxygen in the hot gases.

The great drawback of ceramics as structural materials is their brittleness; unlike most metals, ceramics generally have no ductility or almost none. If this drawback can be overcome by design ingenuity or by making ceramics with greater toughness, a large-volume industry will open for the use of these materials for building engines—more than fifteen million new motor vehicles were sold in the United States in 1988.

#### PROCESSES USED FOR MAKING CERAMIC PRODUCTS

The usual procedures for making metals—melting and casting—won't do for ceramics. Iron can be melted in ceramic-lined containers, but there are no containers for materials such as magnesium oxide, which has a melting temperature of 3175° K.

One process that is used for making ceramics (and also refractory metals such as tungsten) is quite akin to the method used for making snowballs. We start with a powder of, say,  $\text{Al}_2\text{O}_3$  particles and compact them in a die. At this point the component has the approximate consistency of chalk. Then the compacted powder is heated in a furnace to a temperature that is high but substantially below the melting point. In the process, called *sintering*, the powder grows together by the motion of atoms until—ideally—a nonporous solid is formed. Sometimes this sintering is carried out with the powder enclosed in a metal jacket which is surrounded by argon at a pressure of 30,000 psi; this is called *hot isostatic compaction*. Sometimes the powder is first held together at low temperatures with an organic binder (glue) which is driven off at intermediate temperatures; a

Table I

**GOALS OF THE CORNELL CERAMICS PROGRAM****Input:**

- Increase in faculty size
- New equipment
- Visiting industrial scientists
- Visiting professors

**Output:**

- Increased understanding of ceramics science
- More and faster exchange of information
- More ceramicists with B.S. degrees
- Twice as many Ph.D.s by 1992-93
- Further increase in Ph.D. output during 1990s
- Education of Ph.D.s who will have a fuller understanding of how to maximize university-industrial cooperation

further rise in temperature completes the sintering. With this method, sheets of ceramic as thin as paper can be produced.

Other ways of producing ceramics are by precipitation from solution and by deposition from the vapor phase. For example, aluminum, which has a low melting point, can be vaporized in a low-pressure oxygen atmosphere; when the vapor is passed over a cold substrate, a thin film of  $Al_2O_3$  is formed. Alternatively, such a film can be produced by passing a vapor of an organometallic compound, aluminum ethoxide, over a hot substrate; the ethoxide decomposes, leaving an  $Al_2O_3$  film on the substrate, and organic fragments in the vapor flow downstream.

An incredible number of different processes are being used to make ceramics. The number of possible ceramics appear endless, and the properties they exhibit are extremely diverse.

#### THE ORGANIZATION OF CORNELL'S CERAMICS PROGRAM

In 1984, while serving as director of the Department of Materials Science and Engineering, I felt that the time had come to expand our research in the field of high-technology ceramics. It was apparent that new materials with properties not yet achievable would be urgently needed, and that ceramics are leading candidates. In

fact, the federal government was beginning to plan a new initiative in ceramics.

The faculty of our department decided that the proposed ceramics program should continue to emphasize fundamental research—studies that would lead to an understanding of how the properties of ceramic materials can be enhanced. Specifically, we wanted to expand our efforts in areas in which industrial need is likely to be acute:

- ceramic thin films and coatings;
- ceramics for electrical-magnetic and optical applications;
- tough ceramics.

With the help of Professor David Kohlstedt, I prepared a prospectus of a Cornell Ceramics Program that would be jointly supported by industry and government. Subsequently, Provost Robert Barker and William B. Streett, who was then acting dean of the College of Engineering, reached an agreement with our faculty. We were given permission to add three professors if we brought in three industrial sponsors that would each contribute \$1.5 million over a five-year period.

With the help of all the members of our department, but especially those who were already working full-time on ceramic materials, we succeeded in enlisting two excellent companies—Corning Glass Works and IBM. This support, along with funding

from the National Science Foundation, has resulted in an expanded, active program.

As summarized in Table I, we have used the funds obtained from the university, industrial, and government sources to purchase new equipment, add faculty members, and bring in visiting professors and industrial scientists.

#### THE CORE OF THE PROGRAM: THE RESEARCH FACULTY

At the time the program was organized, the department had three faculty members—C. Barry Carter, David Kohlstedt, and Rishi Raj—who were working full-time in the field of ceramics, and others who were working part-time or sometimes on ceramic materials. The program has resulted in an expanded effort by these faculty members, and the addition of two people who already had active programs in ceramics research underway.

Kohlstedt and Raj were carrying out research on the production of ceramic materials (chiefly from powder). Carter was an expert in the use of transmission and scanning electron microscopy for studying the microstructure of materials and the mechanisms of solid-state reactions. We decided, therefore, to seek faculty members who were active in two other areas.

One of the new people, we decided, should be an expert in the study of point defects in solids. This is an important area because the motion of defects is the mechanism essentially responsible for sintering and for reactions in the solid state. The person we found is Rüdiger Dieckmann, who joined us from the University of Hannover in Germany. He brings to us an expertise in handling materials at extremely high temperatures under carefully controlled conditions.

We also sought an expert in the chemi-

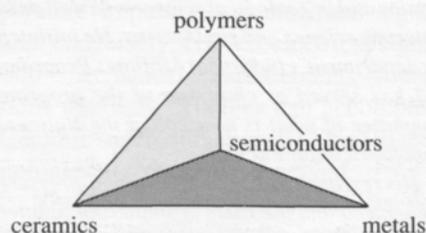
cal synthesis of inorganic materials by processes related directly to the production of ceramic materials. We were fortunate to find a young man, Emmanuel Giannelis, whose experience was in this field; he joined us as an assistant professor.

Cornell faculty members with a primary interest in ceramics include, in addition to these five in our department, James Burlitch (Chemistry), who is working on the synthesis of ceramic materials. A number of other Cornell professors are working part-time in the field; they include Robert Pohl and Albert Sievers (Physics), Robert Buhrman (Applied and Engineering Physics), Frank DiSalvo (Chemistry), and Jack Blakely, Herbert Johnson, Stephen Sass, and myself (Materials Science and Engineering).

#### CERAMICS AS PART OF AN OVERALL PROGRAM

An important aspect of the ceramics research is its integration into the overall program of the department. Ceramics are one of the four kinds of material we study, and research on ceramics is directly connected to work with the other types.

The overall field of materials science and engineering can be thought of in terms of the connecting edges and faces of a tetrahedron:

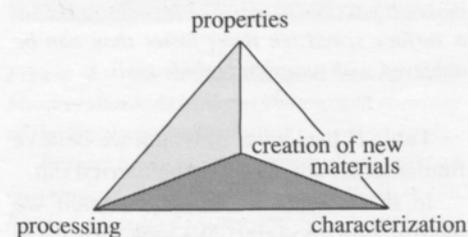


This issue of the *Quarterly* focuses on ceramics (all the professors who are authors are members of the Cornell Ceramics

Program), but we recognize the connections with polymers, semiconductors, and metals. For instance, the superconducting ceramics I have mentioned fall on the ceramics-metals line. Glass-fiber composites—ceramic fibers embedded in a polymer matrix—are “located” along the ceramics-polymers edge. A computer chip comprises silicon (a semiconductor), an electrically insulating barrier of silicon oxide (a ceramic), and electrical leads of aluminum or tungsten (metals) to transmit power and signals; thus the chip involves a semiconductor, a ceramic, and a metal, represented by one side of our tetrahedron.

The value of interplay among people working in different ways with these various materials was recognized in 1961 when the graduate Field of Materials Science and Engineering was formed at Cornell. The field faculty includes professors from our department and from a half-dozen other departments. This facilitates the interaction of polymer scientists with ceramicists, for example, or of semiconductor experts with metallurgists. It is a synergism that leads to more innovation and better teaching and research results for all.

This interplay of disciplines is illustrated by a second tetrahedron representing the scientific approach of materials scientists:



Suppose we make a new material—for example, a high-temperature superconducting ceramic. We will investigate dif-

ferent ways of processing it. We will also experiment to find out how processing affects the microstructure (the positions of the atoms in the crystal structure and the presence of features such as point defects, dislocations, and grain boundaries), and how the microstructure in turn is related to the properties of interest (such as the current-carrying capacity, the superconducting transition temperature, and the mechanical strength).

Eventually, an overall picture begins to emerge and it is seen that certain compositions and defect structures give better properties. Accordingly, changes in processing procedures are made to obtain the best microstructure. What is learned can also be the base for creating other new materials.

#### TOWARD THE HIGH-TECH CERAMICS OF CENTURY 21

Many of the ceramics of the future will be composites.

An example of the possibilities is the recent development of a composite made up of tiny silicon carbide whiskers in a matrix of aluminum oxide—a material hard enough to make a remarkably good cutting tool for machining superalloys such as Inconel. An important new technique was used to make this composite: the whiskers of silicon carbide were grown by submicron fabrication methods. The processing involved hot-pressing a mixture of the whiskers (about 30 percent) with aluminum oxide powder.

This example suggests the wide range of studies that contribute to the development of these new materials. In such a composite, the bonding at the interface of the ceramic whisker and the matrix material is very important; and indeed, the study of surfaces and interfaces is an important area of research in ceramics.



Table II  
**AREAS FOR FUNDAMENTAL  
 STUDIES IN CERAMICS**

- Surface chemistry and physics
- Interfaces: ceramic-ceramic, ceramic-metal, ceramic-polymer, ceramic-semiconductor
- Microstructure, defects, grain boundaries, creep, cavitation
- Multi-component kinetics, dopants in sintering processes
- Coating technologies, sol-gel processes
- Vapor deposition processes: sputtering, CVD (chemical-vapor deposition), MBE (molecular-beam epitaxy)
- Laser and plasma processes
- Colloids, fine powders, whiskers, fibers
- Composites: combinations of ceramics, polymers, metals, and semiconductors
- Ceramic machining, hole-making
- Thermal structures
- Graded interfaces

*Above: A cutter made of a revolutionary new ceramic material is used at Therm, Inc. of Ithaca to machine the alloy Inconel. Left to right are Robert West, director of Therm's Ceramics Division; Arthur L. Ruoff, director of the Cornell Ceramics Program (who served as consultant); and Robert Sprole II, president of Therm.*

*The composite cutter (of silicon carbide whiskers in an aluminum oxide matrix) was produced by hot pressing. This new material makes it possible to machine Inconel 713LC at a surface speed ten times faster than can be achieved with tungsten carbide tools.*

Table II lists areas in which we believe fundamental studies must be carried out.

In the Cornell Ceramics Program we have made a good start. We look forward to contributing significantly to the realization of new high-tech ceramics for the early twenty-first century.

Arthur L. Ruoff, the Class of 1912 Professor of Engineering, organized the Cornell Ceramics Program during his recent ten-year term as director of the Department of Materials Science and Engineering, and is currently serving as director of the program.

Ruoff joined the faculty in 1955 after earning a B.S. degree at Purdue University and a Ph.D. at the University of Utah. At Cornell he is a member of the graduate fields in applied physics and in geological sciences, as well as in materials science and engineering. He initiated his department's Industrial Affiliates Program, and has served as chairman of the program committee of what is now called the National Nanofabrication Facility.

His research is in the areas of high-pressure phenomena and the study of sputtering, sputter etching, and reactive-ion-beam etching. He is currently heading a project to create a national high-pressure x-ray facility at the Cornell High Energy Synchrotron Source (CHESS). Ruoff is a fellow of the American Physical Society.

# ENGINEERING

## CORNELL QUARTERLY



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**Arthur L. Ruoff**  
**Materials Science and Engineering**

**I**t was in 1955—eleven years before the advent of *Engineering: Cornell Quarterly*—that I arrived at the Cornell College of Engineering. What was it like at the college then? The faculty was dedicated to teaching undergraduates; there was little research underway. Usually the parents of the undergraduates paid for most of the students' education. The students understood the source when you quoted from *Hamlet*, cited Seneca or Marcus Aurelius, or referred to classical Greek art or the Renaissance. The administration was capable of providing free parking. At Cornell freedom of speech was practiced and strongly defended and we were free of social engineering.

What is the college like in 1991? We now have a major research effort; there are currently 801 graduate students in M.S./Ph.D. programs in engineering, and 247 in the professional Master of Engineering program. We have new departments, including Materials Science and Engineering, which was established in 1965; in MS&E we now have an undergraduate program (rated first in the nation in the Gourman report) with twenty-five or thirty seniors graduating each year. Our students are bright, but I find they are less knowledgeable in mathematics and liberal arts than students used to be. Parking is inadequate and expensive. The "politically correct" syndrome is prospering at Cornell and is the most serious threat to free speech since the time I arrived on campus.

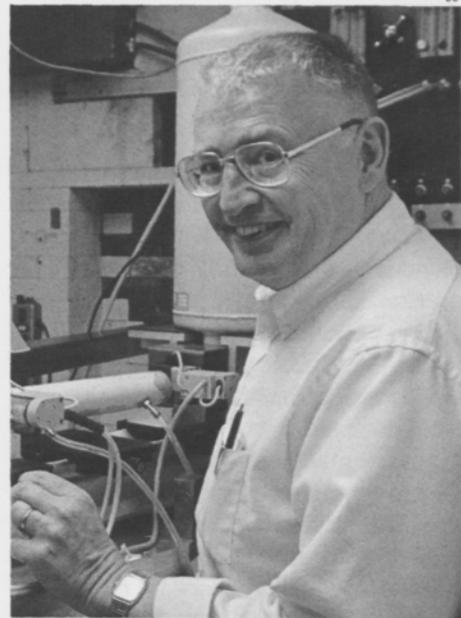
There are now major facilities that make Cornell a mecca for research in materials science. These include the Materials Science Center, the Cornell High Energy Synchrotron Source (a national resource), the National Nanofabrication Facility, and the

*"There are now major facilities that make Cornell a mecca for research in materials science."*

Cornell Theory Center (which includes a national supercomputer facility). These, and the research performed, are primarily supported by the federal government, but close to 20 percent of our research support now comes from industry, much of it via the Cornell Ceramics Program, the SRC Program on Microscience and Technology (Cornell is a SRC "center of excellence"), and the Industry-Cornell Alliance for Electronic Packaging.

In our department we have expertise in ceramics, metals, polymers, and semiconductors, and on materials for structures large and small: composites for airplanes, for example, or carefully made materials for computer chips. We have achieved static pressures greater than those at the center of the earth, carried out x-ray diffraction on samples as small as  $10^{-11}$  cubic centimeter, and studied polymer interdiffusion with use of Rutherford backscattering. Our research is internationally respected.

Of our more than one hundred Ph.D. students, about 25 to 30 percent are foreign—the best and brightest from their native lands. Since many of these foreign students remain in the United States, this constitutes a giant brain drain—a lend-lease in reverse. If better United States applicants were available, we'd take them. Our criterion is: excellence. A great department, a great college, a great university, and a great country owe their eminence to a relentless drive for excellence.



*Arthur L. Ruoff came to Cornell in 1955 as a member of the Department of Mechanics and Materials. He is now the Class of 1912 Professor of Engineering in the Department of Materials Science and Engineering.*

*At Cornell he has served as director of his department and as chairman of the program committee of the National Nanofabrication Facility. He initiated the Industrial Affiliates Program in Materials Science and Engineering, and also the Cornell Ceramics Program, which he directs.*

*Ruoff received the B.S. degree from Purdue University in 1952 and the Ph.D. from the University of Utah in 1955. A specialist in ultra-pressure phenomena, he has published two books as well as several hundred papers. His research includes studies on x-ray diffraction at pressures greater than those at the earth's center.*

*Ruoff has been a visiting professor at the University of Illinois as a National Science Foundation fellow. In 1966–67 the American Society for Engineering Education presented him the Western Electric Fund Award for Excellence in Instruction of Engineering Students. He is a fellow of the American Physical Society.*