Squeezing xenon to a metal, sulfur to a superconductor

Schematic of interdigitated electrodes produced on diamond flat. Actual electrodes have 75 or more fingers. A thin sample is put on top of electrodes. Dashed circles show the circumference of the contact circle when the indentor is applied. Black center circles show two possible cases in which the sample has become conducting.

If you squeeze any substance hard enough to reduce the volume, it is destined to become metallic as the density of electrons is increased. It is also widely believed that the substance will probably become superconducting at sufficiently high pressure and low temperature.

Recently experimenters at Cornell have reported[1] producing metallic xenon—the first rare gas to become a metal. And a group at General Electric and two groups at the Institute for High-Pressure Physics in Moscow have reported superconductivity in sulfur. All the experimenters used hundreds of kilobars pressure.

One of the hopes in such high-pressure experiments is to make metallic hydrogen or oxygen. Theoretical predictions of the superconducting transition temperature of hydrogen range from near absolute zero to room temperature. The dream is that the putative superconducting hydrogen would remain so when the high pressure is removed. But first one would have to achieve and measure reliably static pressures in the megabar range; typical theoretical predictions are that superconductivity would occur at 3–5 megabars.

The idea of making metallic xenon at all would have been astonishing a generation ago, when the closed valence shell of the rare gases was thought by many to preclude chemical interactions. Once rare-gas compounds were produced, it became clear that it might be possible to apply enough pressure to put xenon's electrons into the valence band.

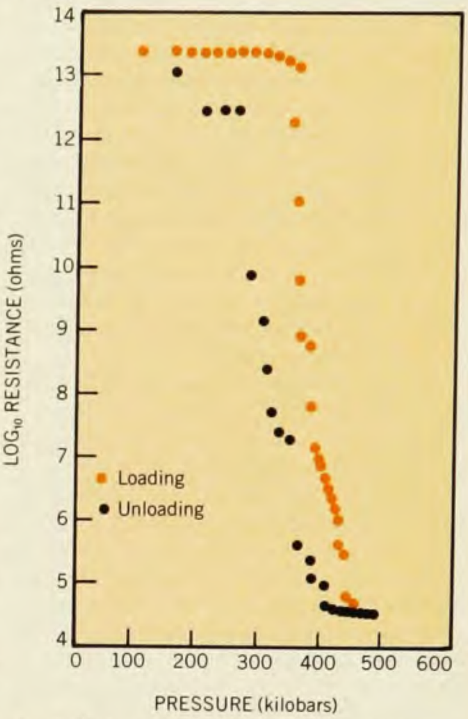
Until the work at Cornell, no element in the rare-gas column of the periodic table had been made metallic. By applying high pressure, experimenters had caused normally nonmetallic iodine, tellurium, selenium and sulfur to become metallic. So it appeared reasonable to Arthur Ruoff and David A. Nelson Jr to try applying pressure sufficient to make xenon metallic.

Ruoff and Nelson used the tabletop, relatively inexpensive, high-pressure apparatus at Cornell, expecting to produce metallic xenon at roughly the same pressure as Ruoff and M. C. Gupta (Cornell) had used[2] in 1977 to produce metallic sulfur.

The device used in the xenon experiment has a flat diamond anvil upon which the experimenters press a diamond with a spherical tip. Ruoff told us that the pressure distribution and maximum pressure applied can be calculated from Hertz contact theory, knowing the elastic constant of diamond, the applied force and the initial radius of the spherical tip. Up to 500 kilobar, this theory has been checked by using Newton's rings, and Ruoff believes the theory holds up to about 2 megabar. The theory assumes diamond's elastic behavior is linear and that the diamond neither fractures nor yields to plastic deformation. One assumes that the diamond's elastic behavior resembles that of germanium and silicon, which have the same covalent bonding and crystal structure.

The experimenters place a very thin sample in the indentor-anvil apparatus and apply force. If the sample is thin enough the pressure distribution will be unchanged, Ruoff said.

One way to measure the conductivity is to put a thin metal coat (about 200 Å) on



Insulator-to-conductor transition in xenon as measured with an electrometer. The transition may be first order or may involve continuous decrease in the band gap, according to the Cornell team, Nelson and Ruoff.

the diamond flat and the indentor and attach leads. Using this technique, Gupta and Ruoff saw no transition in aluminum oxide up to 1.2 megabars, the highest pressure used. When the sample is squeezed, however, one risks pushing the indentor through the sample and producing a short, Ruoff told us. So one could not distinguish between a short and a transition. Had such a reduction in resistance been observed, the Cornell team would have used the non-shorting method[3] described below.

This non-shorting technique employs interdigitated electrodes produced on the diamond flat by photolithography. "Think of the flat as a hand with hundreds of fingers, each 3 microns wide and 200 Å thick." At higher pressures, Ruoff

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expects to make even smaller fingers and spaces using electron-beam lithography. In the present experiment, the team attached leads to the anvil base and then deposited xenon on the anvil by vapor deposition at 30 K in vacuum. Its thickness was typically 1000–2000 Å as measured by a quartz thickness monitor next to the diamond anvil.

One reason to run at 30 K is that the mechanical strength of xenon increases as the temperature is lowered, thus helping to keep the xenon in place.

The Cornell team found that the electrical resistance at 32 K dropped from 10^{13} ohms at atmospheric pressure to about 10^{4} ohms at 330 kilobars with one method. A second method showed the resistivity had dropped to below 0.1 ohm-cm and possibly much lower. In 18 runs, some of the time the resistance dropped sharply, other times with a slight slope. Ruoff told us that he and Nelson can't say if they've seen a first-order transition or a continuous band-gap closing mechanism because it takes so long (weeks) to eliminate hysteresis effects in the experiment.

Sulfur. Comparing xenon with the earlier experiment he had done with sulfur, Ruoff noted that sulfur transformed to a metal at room temperature with the resistance curve having a substantial slope, indicating the effect was a continuous band-gap closing. In 1976, Lalit Chhabildas (Cornell) and Ruoff, using boron-carbide pistons, found[4] the transition began at 175 kilobars; at about 275 kilobars, the resistance had dropped six orders of magnitude. According to Ruoff, this experiment did not achieve the fully metallic state of sulfur.

In 1977, at the Boulder International High-Pressure Conference Ruoff and Gupta, using the diamond indentor technique, reported[2] a resistance drop of 12 orders of magnitude at a pressure less than or equal to 350 kilobars; the calculated resistivity was 0.02 ohm-cm. At the same Boulder meeting, Francis Bundy of General Electric and Keh-Jim Dunn, who was formerly Ruoff's student and is now at GE, reported[5] that sulfur transformed to a metal at room temperature and 475 kilobar; the resistivity was 0.03 ohm-cm.

Ruoff feels that all pressure scales in excess of 200 kilobars are open to question, that it will take several years to sort out the problem. So he feels that the Cornell and GE results are not in disagreement.

The General Electric experiments, done by Dunn and Bundy, use opposed diamond-tipped pistons, which are largely made of tungsten carbide. The very highly stressed regions near the tips are of strongly sintered diamond powder. Between the tapered flanks of the pistons is a button-shaped gasket of pyrophyllite stone (talclike). The GE experimenters put the specimen in a sample holder also made of pyrophyllite. Typical specimen size is 0.06 cm long by 0.025 cm wide by 0.0025 cm thick. At each end is a gold electrode that makes contact with the piston.

The GE group measures the electrical resistance between the two pistons. A typical electrode resistance value is 0.2 ohms, Bundy told us, whereas typical values for the diamond indentors used at the Institute for High-Pressure Physics in Moscow are hundreds of thousands of ohms. The lower background resistance enables the GE group to follow resistivity values of the sample much lower. The Cornell group, Ruoff told us, has a background resistance of 6 ohms.

To calibrate their pressure and resistance measurements, the GE group uses materials such as iron–cobalt and iron–vanadium alloys, in which one can see the transition from face-centered-cubic to hexagonal-close-packed as the resistance increases sharply.

The entire apparatus is placed in a hydraulic press and is clamped in the loaded condition; then the apparatus is removed from the hydraulic press and lowered into a Dewar. Bundy notes that the pressure distribution in the region of the specimen is quite uniform in the GE apparatus. The stainless-steel clamp is temperature compensated so that the load on the specimen does not change during cooldown. Once 4.2 K is reached, the specimen is warmed slowly, and the resistance is monitored.

Bundy told us that in substances such as tellurium, selenium and silicon, they found that when they applied high pressure and lowered the temperature to that of liquid helium or lower, the resistance dropped abruptly from the normal to the superconducting state. However, for sulfur in its "metallic form," he said, the resistance behavior is different. The new GE results on sulfur were to be reported by Bundy on 22 March at the meeting of The American Physical Society in Chicago. For a pressure of 460–480 kilobars, the resistance first drops as the temperature is lowered, then levels out at 100–150 K, and then at still lower temperatures, the resistance increases—a result that surprised Bundy. At 12 K, there is an abrupt change in the rate of increase. At 4–5 K, the resistance increases again. By fitting the curve, considering the resistance of sulfur as consisting of two parts, one being metallic and one being semiconducting, if one subtracts the semiconducting part from the total resistance, there is a jog from 5 to 12 K of the metallic part. This jog is very reproducible, occuring in three runs, each lasting about 2 weeks. The jog looks like that of a smeared-out superconducting transition, Bundy said. However, the data could be interpreted as a structural transformation he noted.

Soviet experiments on superconducting behavior in sulfur were done by two separate groups at the Institute for High-Pressure Physics, where L. P. Vereschagin led the high-pressure efforts until his death last year. In the 20 September 1978 issue of *JETP Letters* (Russian edition), E. N. Yakovlev and his collaborators and V. V. Evdokimova and I. G. Kuzemskaya independently reported finding such behavior.

Yakovlev, using an indentor with carbonado diamonds, finds a drop in resistance at 9.7 K resembling the GE result, Bundy noted, but with higher background resistance. He believes Yakovlev had 400–500 kilobar pressure.

Evdokimova and Kuzemskaya used cemented tungsten-carbide pistons and found that at 200 kilobars, sulfur underwent a superconducting transition at 5.7 K. —GBL

References

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Spin-dependent proton elastic scattering

Recent experiments with the Zero Gradient Synchrotron at Argonne have revealed startling differences in the way protons of different spins scatter elastically. A group from the University of Michigan and Argonne National Lab led by Alan Krisch has found that for protons polarized normal to the scattering plane, elastic scattering at large momentum transfers is about four times more probable for spins parallel than anti-parallel.

The latest experiments were discussed at the 1979 Orbis Scientiae conference on 16 January. Last year the group had already seen[1] the beginning of this dramatic increase at $P_\perp^2 = 4.2\ (\mathrm{GeV}/c)^2$, where the ratio of spin-aligned to spin-opposed cross sections is a bit less than 2. The recent improvements in the intensity (up to 3×10^{10} protons per pulse) and polarization (up to 71% at a beam momentum of 11.75 GeV/c) of the ZGS beam made possible an extension of the experiment to high transverse momentum transfers. By observing scattering at 90° and at the maximum beam energy the group was able to obtain data[2] up to $P_\perp^2 = 5.09\ (\mathrm{GeV}/c)^2$. These energies are the highest that can currently be obtained from the ZGS, Krisch told us, and he has suggested that during its last month of operation the synchrotron's energy be raised so that one can see if the strong spin dependence continues to higher energies. That way