OutPost on the Endless Frontier©

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Squeeze Play

Squeeze play…the explosively-sudden bunting home safely a teammate screaming down the third base line…perhaps the most exquisite maneuver in that most subtle of sports, our National Pastime. But why would we even want to bring up a subject involving a feeble ground ball that travels a mere ten or fifteen feet, in contrast to the current spotlight on the 150 yard trajectories being launched by Sammy Sosa and Mark McGwire that, in addition, usually produce many more runs per incident? Well, to "squeeze" also means to apply pressure -- both the mental variety the two sluggers most assuredly must experience at present, in addition to that which each has applied to 66 baseballs (at least that was the count as we sat writing this edition of *OutPost*!).

Oddly enough, we physicists often feel and utilize these aspects of pressure as well. The former occurs under the intense competition to claim discovery before others (if you don't publish first, you're nothing), and the latter, more pertinent to our present discourse as you will soon see, is to employ application of pressure as a tool for the investigation of matter. The baseball idiom for the signal to bunt the runner on third base home, "putting on the squeeze," was adopted long ago as our jargon for the discipline of high pressure physics. In fact, so useful has this technique been for so many years that, in 1946, it garnered for Harvard physicist Percy Bridgman, the principal pioneer of high pressure experimental methods in the 20th century, one of the very few Nobel Prizes awarded for "lifetime achievement."[1]

Strange and exotic things happen to matter under extreme high pressure, which is loosely defined as anything above 10,000 times that of our atmosphere at sea level.[2] In *OutPost No. 3, "Unidentified Superconducting Objects,"* we pointed out that the core of Jupiter, under a pressure of hundreds of millions of atmospheres, is thought to be hydrogen in a metallic state. In our more mundane terrestial laboratories, by pressing a hydraulic fluid surrounding a given sample contained in vessels made of extremely hard substances like beryllium copper, or "diamond anvil cells," we can achieve static pressures ranging from the above mentioned 10, 000 atmospheres to a million or more, with the capability of simultaneously measuring the structural, thermodynamic and electromagnetic properties of the sample "being squeezed." At around 40,000, the simple element silicon ceases being a semiconductor and transforms into a metallic superconductor, would you believe, and at a million the same thing happens to the normally inert gas, xenon! Don't get too excited -- their superconducting state only occurs below a few degrees above absolute zero and at these very high pressures -- no opportunities here for transmission/distribution cables.

High pressure is also an extraordinarily useful tool for investigating the properties of the more common variety of superconductors. For example, the onset temperature for superconductivity in most "low temperature" superconductors, such as the NbTi wire used in MRI magnets, decreases with increasing pressure, in concert with the Bardeen-Cooper-Schrieffer theory. On the other hand, putting the squeeze on the copper oxide perovskite high temperature superconductors increases their transition temperature, in some instances as much as 15%, an anomalous and completely mysterious finding to date.

So far we have considered only "static" pressure -- that which can be applied constantly. Even higher pressures can be obtained under transient conditions. For a number of years, Lawrence Livermore National Laboratory maintained a "shock wave" facility whereby pressures of several million atmospheres could be reached at wavefronts traveling through samples subjected to pressures produced by exploding military munitions surrounding them. These events could be quite spectacular. Your correspondent once witnessed one "measurement" where a few hundred thousand dollars of test equipment was blown to smithereens. Like a space vehicle launch, it's not a bad idea to get it right the first time. Recently, very high transient pressures have been realized at liquid-solid interfaces through a cavitation effect produced under ultrasonic excitation, high enough to shift the photoluminescence of certain materials about an electron-volt from red to blue, a phenomenon called "sonoluminescence".[3] Finally, in recent years high pressures have been combined with high temperatures to produce in the laboratory new materials stable at ambient in much the same way as geologic conditions in the earth's mantle result in the metal silicates that eventually become mountains. As a matter of fact, about five years ago, we collaborated with geologists at Columbia University and scientists at the University of Maryland to see if we could synthesize novel transition metal oxide (TMO) superconductors using such tools. Unfortunately, we didn't find any, although significant progress was made in TMO solid state chemistry.

There is another way to attain static high pressures in solids -- sort of. When thin films of a given material are formed by vacuum or vapor deposition, quite often the receiving platform or substrate is held at a temperature of anywhere from 200-1000 C in order to enhance mechanical and electrical properties of the deposited layer. Depending upon the relative values of thermal expansion coefficients between substrate and film materials, the film, usually much, much thinner than the substrate, can undergo considerable stresses and strains when cooled to room temperature, resulting, if you will, in "2D high pressure." For example, if we deposit a thin film of a given material on a substrate held, say, at 800 C, whose coefficient of thermal expansion is greater than that of the film being put down, then when both are cooled back to room temperature, the faster contracting substrate will have "squeezed" the film into a state of biaxial compression. Whether this state results in your hitting a home run or into a double play depends on what you're after. The latter described the situation for many years regarding the use of copper instead of aluminum for internal wiring on silicon chips, a difficulty which was recently overcome by IBM using an adhesion-enhancing intermediate step (see *OutPost No. 2, "Faster, Farther, Smaller…Street-Smart Electricity"*), and the former applies to improving the electrical properties in purposely designed "strained layer" bipolar semiconductors, a fabrication technique which may find application to high power thyristors and other FACTS devices.

In the July 30th issue of Nature past, an article[4] appeared reporting several interesting and very provocative results from a European collaboration led by Jean-Pierre Locquet, a former colleague of ours from the IBM Zurich Research Laboratory, the very center from whence Georg Bednorz and Alex Mueller brought the world high temperature superconductivity twelve years ago. Their paper, entitled, *"Doubling the critical temperature of* $La_{1.9}Sr_{0.1}CuO_4$ *using epitaxial strain,"* is an excellent example of applying "2D high pressure" to explore the underlying physics of a frontier material. Moreover, and what attracted almost everyone's attention immediately, including that of some science writers for widely read periodicals, was the finding that the superconducting transition temperature increased, not by 15% as mentioned earlier, but actually ***doubled*** in some samples under highly compressive biaxial strain. There is even a suggestion implicit in one of their tables that Pb-stabilized Bi-2223, or BSCCO, the "utility infielder" of the coming generation of superconducting power devices (see[5] *InSights No. 1, "Superwires: Power in the Fast Lane"*), might be increased from its current 110 K to over 170 K. Such would result in an enormous reduction in refrigeration requirements, especially for cables, perhaps leading to the simultaneous energy delivery of electricity and cooled methane (LNG) which could be used for the cryogen. Tight![6]

This prospect deserves "stealing" a "second" look. The experiment the European team performed was to deposit at 800 C a thin (15 nanometers or 150 Å) of $La_{1.9}Sr_{0.1}CuO_4$ (let's just call this "underdoped-214" from now on) on a thick (probably several millimeters) slab of insulating $SrLaAlO_4$ (SLAO) whose atomic structure closely matches that of 214, but whose thermal expansion coefficient is roughly 25% greater. After cooling this composite structure to room temperature, they found by x-ray measurements that the distances between atoms in the plane of the film were about 0.7% smaller than normal for 214, implying a "2D pressure" condition of some 50,000 times atmospheric. Of course, this pressure would increase even more as the sample was cooled to undergo measurement of its superconducting properties.

> *Historical Digression:* Doped-214 was the material discovered by Bednorz and Mueller in 1986 that became the template for all subsequent high temperature superconductors that followed. By "doped" we mean substitution of a divalent alkaline earth element like Ca, Ba or Sr for trivalent La in "pure" 214 which results in the production of mobile positive charge, "holes," much like that which occurs when one puts boron in silicon. These positive charges then bring on the superconducting state as the temperature is lowered. It turned out that a ratio $La_{1.8}Sr_{0.2}$ is "optimum" in that the highest transition temperature, 40 K, was obtained at this concentration. Now, as the strontium concentration is reduced, so is the transition temperature, and, at the concentration used for the Locquet, et al., film, $La_{1.9}Sr_{0.1}$, i.e., "underdoped-214," T_C is usually only 25 K. One more matter. In superconductivity physics parlance, the term "bulk" is used to describe the condition when the superconducting state pervades 90% or more of the sample

> as determined by its diamagnetism. Any fraction appreciably less implies the presence of some sort of inhomogeneity. "Underdoped-214" is invariably non-bulk compared to "optimally-doped-214."

The Europeans reported their underdoped-214 film to have a T_C of 49 K, almost twice that of an equivalent ceramic sample made by the usual method of calcining metal oxide precursor powders into pellets. The authors attributed this increase in transition temperature as due to the 50,000 atm biaxial pressure introduced during growth of their film, and, by extrapolation, might lead to similar dramatic increases in all other copper oxide high temperature superconductors, including, as mentioned, those utilized in wire for power applications.

However, *OutPost* has several serious concerns with these conclusions.

- First of all, the only sample whose superconductivity was measured was the underdoped composition. We would have been much more impressed had the doubling effect been observed in optimally-doped 214, driving it from 40 to 80 K. Locquet, et al., reported difficulty preparing mechanically stable films with that La/Sr ratio.
- The authors maintained their sample was "bulk" as defined above, yet presented no commonly accepted experiments to substantiate this claim. Given the extreme thinness of the film, the standard magnetic measurements would have been difficult, but not impossible.

The chemistry and physics of copper oxide perovskites are, as we said about the game of baseball, complex and subtle. The superconducting transition temperature of the entire family depends delicately on doping and oxygen content. Oxygen especially is one of the most pernicious of elements to detect…only neutrons pitched at it are hit back with any regularity. Given this lineup, *OutPost* sees at least two plausible alternatives to explain the European observations on their one sample of underdoped-214, especially in the absence of supporting data that said sample was bulk. Evidence is accumulating that superconductivity in underdoped specimens occurs inside domains, or "stripes," within the sample and is not pervasive. The application of biaxial stress could move the doping levels within such domains toward optimization and thus raise T_C above, but not much above, the maximum 40 K. Moreover, and perhaps more likely, the two-dimensional nature of the squeeze on the atomic structure of 214 may allow for the incorporation of more oxygen than normally allowed. Imagine the temporary shape taken on by a baseball when struck by a hitter with the power of McGwire. The normally spherical ball is compressed around its equator and its polar axis expands…becoming the egg-like prolate spheroid you studied in high school geometry. We know some extra oxygen can enter in between the copper oxide planes under ordinary conditions, and probably even more in the extra space created perpendicular to the squeeze. In fact, a collaboration led by your correspondent found in 1987 that small amounts of additional oxygen in 214 can raise its onset of superconductivity to 41-42 K without any need for doping at all with alkaline earths.[7] Perhaps this effect is "the play of the day" which explains the European group's results.

The Locquet, et al., Nature article presents an interesting game plan. But will it develop into a new grand slam for power applications of superconductivity? Most likely not, even though it ain't over 'til the last batter's called out. With this sixth edition of *OutPost*, the reader has probably noticed we have had, from time to time, a penchant to close by quoting appropriate lyrics from popular music of our era. This time we find quite to the present point some lines penned by John Fogerty, songwriter and frontman for the great old Credence Clearwater Revival band, and found in his tribute to baseball, *Centerfield*: "Put me in, Coach, I'm ready to play…Today." But, alas, as far as the next "run to be batted in" for power applications of superconductivity is concerned, we have to conclude from the July Nature paper there's still nobody on third and no pinch hitter in sight…no Big Mac or Slammin' Sammy to hit even a sacrifice fly, let alone execute a squeeze play.

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[1] Bridgman's Nobel citation read, essentially, "…for the invention of high pressure apparatuses and the discoveries he subsequently made in high pressure physics." More typically the Nobel Prize in Physics is given for a specific discovery or event, as exemplified by Einstein's in 1921: "…for his discovery of the laws of the photoelectric effect." Of course, Albert undoubtedly would have qualified for at least three or four more, had he still been around once John Bardeen broke the "single award" barrier in 1972.

[2] For purposes of calibration, the pressure inside a bottle or can of beer (unshaken) is around 1.5 atm, champagne 3-5, your auto tires about the same, and your outdoor barbecue propane tank perhaps as high as 10.

[3] A note of caution. There are a few fringe proposals making the rounds purporting temperatures and pressures may be achievable by sonoluminscence high enough to shift the x-ray emission spectrum of common elements (in the several kilo-electron-volt range) to gamma rays (mega-electron-volts), a 3-4 orders-of-magnitude increase…quite a stretch considering the observed change in visible light is only about a volt. If this could actually be done, energies would be produced comparable to those found in hydrogen isotope fusion and then you-know-what happens. If any of these schemes cross your desk, please contact *OutPost* before pulling out your checkbook.

[4] J.-P. Locquet, et al., Nature **394**, 453 (1998).

[5] http://www.epriweb.com/srd/outreach.html.

[6] "Tight"…a fashionable expletive-of-the-day, courtesy of Pamela L. Grant, 9th Grade, Leland High School, San Jose, CA. Synonymous with "cool," "wow."

[7] P.M. Grant, et al., Phys. Rev. Letters **58**, 2482 (1987).