OutPost on the Endless Frontier©

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Unidentified Superconducting Objects

My daily trip from home to EPRI is approximately 30 miles or about an hour, not of unusual distance or duration for an inmate of Silicon Valley. The California commuter's constant and ubiquitous companion is his car radio whose program content can range between the extremes of Howard Stern to rap rock. Typically, my habit is to alternate between just two –a Spanish-language music station that identifies itself delightfully as "Radio Romantica" and the CBS national network news. One morning, about a year ago, as I pulled into our Palo Alto parking lot, I was tuned to CBS and caught the following terse "sound bite" just before stepping out of my car, "Today French scientists announced the discovery of superconductivity at room temperature in a black powder compound, a feat never before achieved."

Early USO Sightings

After the original discovery of perfect conductivity, or superconductivity, in mercury metal at 4.2 K in 1911, there began an intensive search throughout the remainder of the century for materials superconducting at higher temperatures, and therefore potentially easier to apply as a result of reduced refrigeration requirements. The dream quickly became to discover a "room temperature" superconductor that would usher in an age of lossless transmission of electrical energy and vast increases in the efficiency of its generation and end use. The zeal with which this goal was pursued produced, from time to time, like the newspaper obituary of Mark Twain, premature reports of its arrival. This writer had made it his practice for many years to investigate as best I could these incidents. Without exception, my colleagues and I found them to be either irreproducible events or mistakes. A term came into general use, unidentified superconducting objects, or USOs, whose acronym is a Japanese word meaning, roughly, "error." How appropriate in retrospect. However, I must stress that there exists no physical reason why one cannot have superconductivity at any temperature (neutron stars are believed to possess a superconducting state at 10^9 degrees, a temperature high enough that the actual units don't matter any more!) and the sound science practice should be to take all USO "sightings" seriously until proven otherwise

Another French Revolution – Quatorze de Juillet ou Dix-huit de Brumaire?

So what about this French report? Does it presage a permanent revolution or another futile storming of the barricades?

A quick call to CBS resulted in a fax of the Reuters news wire on which they had based their radio report. Of course, I immediately distributed the news to a number of colleagues both is the US and Europe with the obvious inquiry, “What’s up besides maybe the transition temperature?” After a few days, the following picture emerged.

A day or so before the CBS report, a graduate student, working at the National Institute for Applied Science, INAS, in Lyon, France, had presented his thesis defense on measurements performed on a sample containing the elements lithium, beryllium and hydrogen and believed to have the chemical formula Li_2BeH_4. Present in the room was a reporter for the local newspaper, Lyon Figaro, a situation I find rather unusual. It has not been my experience that journalists generally attend such events (none were at mine!) unless “tipped off” that something interesting is about to be revealed. The student reported two results, one the observation of magnetic hysteresis, this experiment actually having been performed at a CNRS lab near Paris, and a specific heat anomaly, both occurring at 80 C, which he stated were consistent with superconductivity. They are also consistent with a structural and/or magnetic phase transition, or even decomposition. The next morning, a rather sensational article appeared in Lyon Figaro which was picked up by Reuters and the “cat was out of the bag.”

The sample measured in Lyon was made in a laboratory of the French Atomic Energy Commission (CEA) near Paris. Due to its instability in air, the compound, described as a white (not black) powder, was sealed in an ampoule before being sent for the magnetic and specific heat measurements. Presumably the necessity for such enclosure is the reason structural and electrical measurements were not performed. Why the Reuters wire described the sample as black remains a mystery to this day.

Bad Guys Wear White

The white color description, which subsequently turned out to be correct, was an important clue. It’s not generally appreciated that much can be inferred about the physical properties of a material from its color perception. A white powder usually indicates the presence of microscopic transparent crystallites...think of table salt, sugar and snow, for example. The physiological perception of whiteness comes from the enormous total internal reflection of all visible wavelengths by the randomly oriented transparent crystallites. The transparency in turn infers the material is insulating with a large band gap or optical excitation energy well into the ultraviolet or beyond. The reflected color of metals, on the other hand, depends fundamentally on the density of screened itinerant electrons or holes, which manifests itself through the position of the Drude plasma frequency or energy, below which light is highly reflected, with respect to the visual response of the eye. Thus, some metals, e.g., high temperature and organic superconductors, appear black in powder form because their carrier density is not high enough to reflect at wavelengths shorter than the infrared, so most visible light is absorbed. High carrier density metals, such as gold, silver, copper, etc., exhibit a variety of colors as their plasma frequencies span the visible spectrum (exercise for the reader: why are there no green metals?).

Therefore, the white color of the French sample alone indicates that it is an insulator and not a metal, a powerful argument that neither can it be a superconductor.

The Ultimate Metal

Why would the French, or anyone else, be interested in looking at LiBe hydrides as possible candidates for high temperature superconductors? For one very good reason. Pursuit of the ideal, perfect metal has long been one of the fundamental goals of condensed matter physics. Its material realization has most frequently been visualized as "metallic hydrogen," essentially one electron per simple cubic cell. A number of theoretical studies suggested that metallic hydrogen, if it could actually be achieved, might be a very high temperature superconductor. A major obstacle, however, was that extremely high pressures, on the order of millions of atmospheres, would be required to compress gaseous hydrogen into solid form (it is thought the core of Jupiter may indeed be solid hydrogen, presenting a formidable challenge to anyone wanting to make electrical measurements!).

Given these difficulties in its direct preparation and measurement, the search for metallic hydrogen inspired a number of investigations for its possible existence in the ambient solid state, especially in metal hydride compounds. Whereas the simplest metallic hydrogen model derived from alkali metal analogs, hydrogen as an anion has a much larger ionic radius than H^+ and the thought was perhaps electron delocalization was more likely to occur in hydrides, especially those with significant concentration of such cations. Hydrides of palladium were particularly intensely studied...the most infamous consequence being the cold fusion imbroglio. However, PdH did exhibit a Tc of about 10 K, surprisingly high, but unlikely due to the presence of hydride-borne carriers.

In 1968, two British chemists, N. A. Bell and G. E. Coates, published their synthesis of two hydrides of lithium and beryllium, nominally identified as $LiBeH_3$ and Li_2BeH_4. These compounds decomposed rapidly in air and at slightly elevated temperatures...one of the secondary phases, BeH_2, can undergo violent decomposition and has been considered as a potential rocket propellant. There matters sat for almost twenty years. A casual literature search showed no apparent follow-up by the chemical community, and the report seems to have totally escaped the notice of physicists, that is, until January, 1987, when A. W. Overhauser of Purdue University speculated that “these compounds, if metallic, may manifest the high temperature superconductivity often envisioned for metallic hydrogen.” It was this speculation that encouraged the French group to experimentally search for superconductivity in the lithium beryllium hydrides.

Rock On, Baby!

All attempts at verification of the Lyon measurements and their interpretation known to *OutPost* over the past year have been negative and indeed reveal insulating behavior. It is almost certain now that the Lyon observation is an artifact. It is easy to have a smug and condescending attitude toward the naiveté surrounding premature reports of unidentified superconducting objects such as this latest. But, really, the French graduate student and his advisors deserve much praise for their attempt to probe unusual material paths for interesting physical properties...this is just how new superconductors are discovered. As the discovery of superconductivity in copper oxide perovskites in 1986 taught us, it can happen and it will happen again…let's keep the faith and keep looking.

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