Front. Phys., 2011, 6(4): 347–349
DOI 10.1007/s11467-011-0226-8

PERSPECTIVE

Gifts from the superconducting curiosity shop

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Received October 16, 2011; accepted November 20, 2011

Superconductivity has just celebrated its 100th birthday, and yet despite its advanced age it has never been more alive. Given that most subfields of materials physics have a half-life of about seven years, what accounts for the enduring popularity of superconductivity? What is it about superconductivity that continues to fascinate?

The answer, of course, is that "it's the materials, stupid." And especially the exciting new materials that serve to periodically re-energize the field. Superconducting materials display a nearly zoological level of diversity and complexity, ranging from elemental metals to multinary intermetallics, Zintl phases, organics, and oxides. Some are good metals, some are "bad" metals [1], some are semimetals, and some are barely metals at all. The interplay of magnetism and superconductivity is deeply mysterious, as is the relationship between ferroelectricity and superconductivity [2]. Dimensionality also seems important in that many of the most interesting superconductors have layered crystal structures, and yet this, too, is mysterious in that there seems to be no good way to quantify the "2D-ness" of a system in a consistent way. Further mysteries abound, especially when one starts to think about superconductors from a chemical point of view. Why is it, for example, that some of the most interesting superconductors (e.g., La_2CuO_4 and $BaFe_2As_2$ families) have both ionic and covalent bonding in the same material? This is reminiscent of the Zintl concept, in which electrons from element A are donated to element B, which then uses the donated electrons to form covalent bonds (NaTl is the classic example) [3].

Although it is clear that new materials are the lifeblood of superconductivity, it is not clear where future materials will come from as we have no good heuristics (rules of thumb) for finding interesting new superconductors. It is not for lack of trying. In the 1950s (pre-BCS) Matthias developed the first set of guidelines for finding new superconductors by emphasizing certain regularities among superconducting elements and compounds, especially the valence electron/atom (e/a) ratio. In a 1955 paper Matthias demonstrated that a universal curve could be drawn for T_c as a function of (e/a) for elements and simple compounds with a maxima at 5 and 7 and a minimum at 6 [4]. Although this simple rule worked well for elements and simple binaries, it eventually became clear that the rule failed for more complex ternary compounds like the Chevrel phases. In 2001 Pickett observed that many of the newer superconductors that violated Matthias's rules had several things in common: "(i) must be multicomponent — more than a binary; (ii) at least one site should have variable occupancy ("dopant"); (iii) large electronegativity difference between constituents; (iv) proximity to a magnetic or insulating phase; (v) mixed antibonding bands at the Fermi level; (vi) there are favorable electron/ion ratios." [5] It must be said that although these new rules have stood up rather well so far, they have limited predictive power and are not terribly helpful for finding new materials. In fact, theory has generally not been of much help in finding new superconductors. This has been emphasized by Fisk, who has pointed out that the graph of maximum T_c vs. time "sails through 1957 BCS without a glitch." [6]

It must be recognized, therefore, that at least for now we are dependent on serendipity for the discovery of new superconductors. This is why new families of superconductors so often seem to come from "out of the blue." This is actually a dangerous situation, for the kind of exploratory synthesis that is required to find new families of superconductors is losing ground to a "materials-by-design" mindset in which progress can be "directed" by "high throughput" computing. Something similar has happened in drug research. Writing in the Financial Times, Shaywitz and Taleb explain that the dwindling drug pipelines can be understood as a failure to capitalize on "positive uncertainty," or serendipity:

> . . . The process of drug development is also very difficult to predict, because of both our limited understanding of disease and our inevitably imperfect understanding of the effect any new compound will

> have on the body. While design played a pivotal role in the development of effective HIV drugs, other modern medications were discovered in the old fashioned way: by accident. Viagra, for example, was originally developed as a treatment for chest pain.
>
> In the face of declining productivity, pharma companies have been trying to boost output by increasing efficiency, narrowing their focus to a handful of disease areas, shelving safe but ineffective compounds without fully exploring their scientific potential and trying to ensure that each project the company is working on is carried out with a clearly defined market segment in mind. Unfortunately, for new medicines in particular, this strategy often fails significantly to reduce exposure to negative uncertainty — all the bad things that can happen during drug development — and eliminates much of the exposure to positive uncertainty (serendipity) that remains so vital [7].

I think the lesson that should be drawn is that there should always be room for serendipity in science, and particularly in the search for new materials.

A "curiosity shop" conjures up the image of a large, disorganized, and slightly musty store in an older part of town that has accumulated so many odds and ends over the years that nobody is really sure what is in there anymore. I think in many respects such an image is fitting for the vast literature on superconductivity, and I thought I would briefly mention three of the more unusual superconductors I have come across while rummaging around there. These superconductors are not fashionable and do not have very high transition temperatures, but they are fascinating nevertheless because they are oddities and serve to highlight the sheer chemical diversity of superconducting materials.

The first one is a silver clathrate salt, $Ag_7O_8NO_3$. Superconductivity in this material (and some relatives) was reported by Robin and co-workers in 1966 [8]. The argentic oxide salts $(Ag_7O_8)^+X^-$ ($X^- = NO_3^-$, HF_2^-, BF_4^-, F^-, ClO_4^-) are cubic clathrates consisting of face-sharing, 26-sided Ag_6O_8 polyhedra with the anions located in the centers of the polyhedra. The T_c's of these materials are very low, the highest being $1.0 - 1.5$ K for $X^- = NO_3^-$ and HF_2^- [9].

These materials are interesting for a couple of reasons. First, silver is immediately under copper in the periodic table and the silver is mixed valent just like copper is mixed valent in the cuprate superconductors. Furthermore, the coordination of the silver is 4-fold square planar, again like the cuprates. After that the analogy breaks down, because in the silver clathrates the square-planar units link to form clusters, which in turn link to form a cubic structure. The other reason these materials are interesting is that they are the first examples of superconducting metallic clathrates. Clathrates have interesting lattice properties because the caged ion has a much lower characteristic vibrational frequency than atoms making up the cage. This is readily apparent in specific heat experiments, where a low frequency Einstein contribution is clearly visible. Other clathrate (and crypto-clathrate) superconductors include $Al_{10}V$ [10], KOs_2O_6 [11], and Ba_8Si_{46} [12].

The next one is polysulfur nitride $(SN)_x$, which was discovered to superconduct at 0.26 K by Greene and co-workers in 1975 [13]. $(SN)_x$ is a quite curious material because it is an inorganic polymer, and in fact the first polymer discovered to superconduct. It is highly one-dimensional, and grows as golden fibrous crystals with metallic luster. The fibers are several hundred Angstroms across and are composed of highly oriented $(SN)_x$ chains. Polysulfur nitride in some sense presages the explosion of interest in low dimensional metals, organics, and even nanowires. It is also notable that two of the precursors in the synthesis, S_2N_2 and S_4N_4, are both explosive and thus great care must therefore be taken in the preparation of $(SN)_x$.

The third material is a superconductor discovered in 2007 by Hosono's group, $12CaO{\cdot}7Al_2O_3{:}e^-$ [14]. By a chemical reduction treatment oxygen ions in sub-nanometer cages are removed, allowing doped electrons to occupy the former oxygen sites. Hosono calls the resultant material an inorganic "electride," which is typically composed of an anionic electron and the cationic framework. As the authors amusingly point out, oxides such as Al_2O_3 are typically used as "architectural materials." In other words, this material is essentially superconducting cement, and is about as far away from Matthias's rules as it is possible to get.

Perhaps the secret to eternal youth is simply to remain curious? In that case the future of superconductivity looks bright because there is little doubt that new superconductors will continue to be found as long as we continue to search for them.

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