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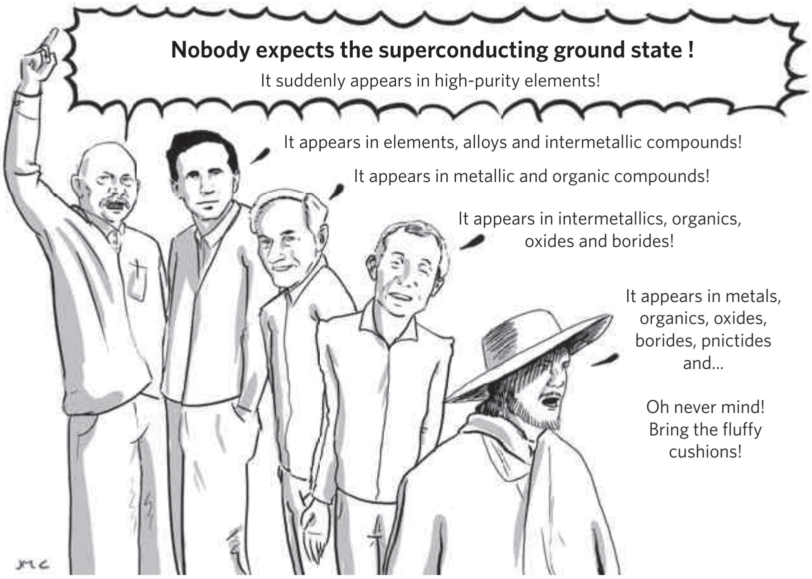
Still alluring and hard to predict at 100

Paul C. Canfield

Superconductivity has gone from a rare event to a ground state that pops up in materials once considered improbable, if not impossible. Although we cannot predict its occurrence yet, recent discoveries give us some clues about how to look for new — hopefully more useful — superconducting materials.

Birthdays are always a time for introspection and, given the number of fingers humans generally have, a one hundredth birthday is especially so. Almost exactly a century ago, in April 1911, the laboratory run by Heike Kamerlingh Onnes at the University of Leiden discovered a sudden transition to zero resistance in high-purity mercury on cooling through 4.2 K. At the time, Onnes was basking in the glory of winning the race to liquefy helium (see ref. 1 and references therein) and was using this new phase of helium to study the behaviour of matter cooled to newly accessible, lower temperatures. The reason that Onnes was measuring the temperature-dependent electrical resistivity of mercury was to test the proposed 'death of conductivity' or 'freezing out of carrier motion' that had been proposed by Lord Kelvin as the fate of electrons when absolute zero was approached[1]. Mercury, given its high vapour pressure, allowed for purification via distillation. The sudden phase transition to an infinitely conducting state was an unimagined result. This first, surprising, appearance of superconductivity was a herald of things to come. Over the ensuing century superconductivity would continue to pop-up in what were thought to be extremely unexpected places, repeatedly: in organic compounds, in oxides, in magnetic compounds, in an overlooked boride and most recently in a whole family of FeAs- and FeSe-based compounds. At this point it is sort of like the old *Monty Python's Flying Circus* 'Spanish Inquisition' skit[2,3], with everybody expecting superconductivity to appear more or less wherever it wants to (shown apocryphally in Fig. 1).

The simple fact that researchers continue to be surprised by superconductivity's appearances is evidence that we still do not have a firm grip on what is needed to give rise to this intriguing state. We just celebrated the fiftieth anniversary of the BCS (from Bardeen, Cooper and Schrieffer) theory, which explains



JACOB M. CANFIELD

Figure 1 | The surprising nature of superconductivity. Like the *Monty Python* 'Spanish Inquisition' skit[2,3], superconductivity has repeatedly popped up in unexpected places.

the condensation of electrons into the zero-resistance state via the formation of electron pairs (known as Cooper pairs) through the interaction with lattice vibrations (phonons), and explains the temperature, magnetic field and frequency dependences of superconductivity in great detail. But unfortunately this theory has, so far, failed to offer any significant guidance for the prediction or discovery of new superconducting compounds. This shortcoming has been further highlighted by the discoveries, in the past few decades, of superconductors that may well be forming Cooper pairs via yet-to-be-understood mechanisms other than electron–phonon coupling. In the absence of strong theoretical guidance as to where to search for new superconducting compounds we are left with empirical rules, or in some cases gestalt feelings, for how to try to find new superconductors. The discovery of new superconductors is vital because it is a ready supply of new superconducting compounds that will (hopefully) lead to the missing insight into what key features are needed for superconductivity, as well as serve as the pool from which new, practical (industrially useful) superconductors will spring.

This commentary presents my sense of how we can try to find these new superconductors based on what we have learnt so far. Some of these feelings are hardly unique and, in some cases represent a consensus view across the field; others may be more idiosyncratic and represent my own take on how to prioritize a search in a multi-dimensional, composition/interaction phase space. (Or, to phrase this more in the terms of my theoretical colleagues, how to identify and order terms in a multi-component, yet-to-be-fully-understood, Hamiltonian.) To put these ideas and feelings into some perspective it is useful to observe a few more anniversaries and discuss the cuprate high-transition-temperature (T_c) superconductors (now celebrating their twenty-fifth), MgB_2 (now at its tenth), as well as the most recent family of interest, the FeAs- (and related FeSe-) based compounds. These newcomers can be compared to the grand old dame of practical superconductivity, Nb_3Sn, which is a bit over 50 years old now. At the risk of not inviting every class of superconducting compound to this little party, we need to acknowledge that there have also been interesting discoveries in heavy fermions (in particular $CeCoIn_5$), C_{60} materials, and so on, but for this commentary I will focus the discussion more on compounds that were (or still are) potentially practical superconductors.

What is our goal?

Although superconductivity in Nb_3Sn was discovered in 1954 (ref. 4), it took decades to have affordable, reliable magnets made out of it. Part of this delay was associated with mastering the metallurgy associated with forming reliable Nb_3Sn wire. The other part of it was associated with improving the upper critical field (H_{c2}, above which superconductivity disappears) to its current high of ~30 T at ~2 K (see Fig. 1 of accompanying commentary[5]) while simultaneously optimizing the critical-current density (J_c, the maximum current density that can flow without dissipation)[6]. Nb_3Sn can now be considered fully optimized and is one of the industrial standards for superconductivity. Also shown in Fig. 1 of ref. 5 are the $H_{c2}(T)$ data for carbon-doped MgB_2 as well as one of the recently discovered FeAs-based superconductors, $Ba_{0.55}K_{0.45}Fe_2As_2$. As can be seen, the $H_{c2}(T)$ plots for both MgB_2 and $Ba_{0.55}K_{0.45}Fe_2As_2$ exceed Nb_3Sn in both temperature and field. MgB_2 wire technology is now being developed with the goal of having magnetic resonance imaging (MRI) magnets that can operate at 20 K instead of 4.2 K and, if J_c values of $Ba_{0.55}K_{0.45}Fe_2As_2$ can be improved (always a big 'if'), the fact that $H_{c2}(T = 20\ K)$ is nearly 40 T (and also essentially isotropic[7]) makes the FeAs-based compounds of great technological interest.

With data from both C-doped MgB_2 and K-doped $BaFe_2As_2$ in mind, it is useful to try to outline what we are looking/hoping for. Most researchers would be happy with either (1) a better example of a known class of superconductor, for example an FeAs compound with significantly higher values of T_c or J_c, or a compound that brings phonon-mediated superconductivity a significant step beyond MgB_2's T_c of ~40 K without significantly increasing the cost of fabrication, or (2) the discovery of a new class of superconductor (for example, a Co- or Ni-based high-T_c family). This being said, it should be pointed out that over the past two decades, based to a large extent on the problems associated with making affordable and reliable CuO-based high-T_c wire/cable, a feeling that some T_c can be sacrificed for isotropy and processability has emerged. Although improvements in T_c often get the most attention, other improvements, such as decreasing $H_{c2}(T)$ anisotropy, improving critical-current densities and, very importantly, finding a superconductor that is cheap and easy to make and form into wires, are arguably as, if not more, important.

Where to look?

There are many ways to segregate superconductors: elemental or alloy, inorganic or organic, clean or dirty, type I or type II, *s*-wave or complex symmetry, practical or non-practical. Given that superconductors now being considered as potentially practical come from both low-T_c and high-T_c families, it is fair to ask: "what areas of phase space should be the focus of searches for new and hopefully more useful superconductors?" This question brings us to an operational classification of superconductors. In terms of looking for new examples of superconductors, a useful division can be based on a modification of the low-T_c/high-T_c classification, focusing on the compositional nature of the members of each class. As examples we can take Nb_3Sn, RNi_2B_2C and MgB_2 (refs 4,6,8,9) on one hand and the CuO- and FeAs-based compounds[10,11] on the other. The first class manifests robust superconductivity for well-ordered, stoichiometric, line compounds. The second class has superconductivity that emerges from compounds that, when examined in their pure, stoichiometric form, are neither superconducting nor even very good metals (if metals at all). Members of this second class of materials only superconduct when modified (usually by substitution) in a very specific, idiosyncratic, way. For example, superconductivity can appear in $BaFe_2As_2$ when Co or Ni are substituted for Fe, but not when Mn or Cr are substituted; superconductivity in CuO-based compounds, on the other hand, is essentially destroyed if any transition metal is placed on the Cu site, but is stabilized by control of oxygen stoichiometery or doping with alkali earth elements. For lack of a better term, we can think of these two classes as manifesting conspicuous versus obscured superconductivity. Each type of these classes of superconductors has specific search algorithms associated with it.

For conspicuous superconductors the search is easier in practice, but a large swathe of the simple-to-access phase space has been explored over the past 100 years. When a material superconducts as a well-defined fully ordered line compound (that is, with full occupancy of each crystallographic site by a single element), it will manifest superconductivity even if it is a minority phase of a multi-phase sample. Given that superconductivity is relatively easily detected in simple transport measurements, detecting superconductivity even in minority phases is not difficult. The key question for such a search is: "where to look?" From a low-T_c perspective there is a problem in optimizing density of states at the Fermi surface, Debye frequency and electron–phonon coupling. As MgB_2 so clearly demonstrated, very high values of T_c can be achieved by ignoring the density of states and focusing on Debye frequency and electron–phonon coupling[9]. On the other hand, many of the earlier low-T_c compounds used transition-metal *d* states to increase T_c values. At this point researchers are: (1) looking for other low-density-of-state high-T_c-value compounds similar to MgB_2, often by using compounds rich in B and/or C (for example, metal borides with zero-, one-, or two-dimensional arrays of boron that resemble the carbon backbones of organic molecules or graphitic sheets and thereby preserve the σ and π bonding/banding that was so vital in MgB_2), and (2) looking more in the less-explored N, P, As and S, Se, Te columns with varying combinations of transition metals to increase the electronic density of states.

For the class of obscured superconductors, the search is much harder. First a parent compound, or set of parent compounds, has to be discovered and then the parent compound has to be doped/modified in the correct way. It is clearly improbable that this can happen by accident or as part of a broad survey of multi-phase samples, especially if we consider that the parent compounds do not have to be superconductors, good metals or even metals at all. In essence, the likelihood of chance discovery is the product of two small numbers. This may well be the reason why, even 100 years after the discovery of superconductivity, we have only two main classes of this type of superconductivity.

To search for new examples of this second class of superconductor in a vaguely systematic manner, an assumption about the nature of the superconductivity, or at least about the nature of the obstructing phase existing near (and possibly related to) the superconductivity has to be made. Based on the generic phase diagrams for the CuO- and FeAs-based superconductors shown in Fig. 2 (refs 10,11), the most obvious assumption would be that an antiferromagnetic parent compound is needed and that the antiferromagnetism should be suppressible but lingering. Over the next few years, as many research groups slowly turn from the FeAs-based materials and start to look for other examples of superconductivity, the idea that the delocalization of long-range antiferromagnetic order may be a way forward will be an influential one. In this case the materials will very likely contain transition metals, so as to provide the type

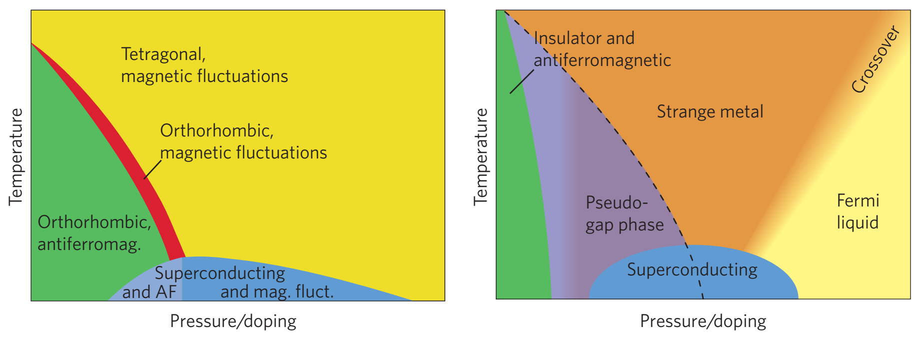


Figure 2 | Similar phase diagrams. Generic phase diagrams for the FeAs-based (left) and CuO-based (right) high-*Tc* superconductors (based loosely on refs. 10 and 11) show that in both cases superconductivity emerges once a neighbouring antiferromagnetic (AF) phase is adequately suppressed.

of antiferromagnetism that can be tuned into superconductivity. One of the greatly liberating aspects of the discovery of the FeAs-based superconductors is the fact that now we are not limited (by prejudice) to feel that Cu or Fe are the only transition metals that are likely to give rise to new superconductors; Fe, Co, Ni, Cu as well as a selection of other 3*d*, 4*d* and even 5*d* transition-metal-based materials will undoubtedly be examined.

The past few decades worth of research have also taught us that being able to narrow the band from that of a simple metal is a vital part of finding the right type of antiferromagnetism, so many of the new materials that will be examined will also contain chalcogenides and pnictides, to adjust the band width. Finally, alkali or alkali earth elements will often be present to tune band filling, given their ability to substitute for a wide number of other elements and yet be fairly invariant in their own valancy.

Going strong into second century

Given the discoveries of MgB_2 and FeAs-based superconductivity over the past decade[12,13], and given renewed experimental efforts as well as funding support, I am very optimistic that we (humanity) will discover further examples of new, and even improved, superconductors. One can hope that there will be further examples of innovations in both classes: more MgB_2-like surprises as well as examples of other transition-metal-based families of high-T_c-like materials. Ideally, there indeed will be nothing special about Cu or Fe and, with time and patience, we will find further examples of obscured superconductivity in compounds that have a wide variety of transition-metal elements (hopefully even expanding from the current 3*d* shell to 4*d* or even 5*d* elements). Remarkably, even 100 years after the discovery of superconductivity, these are very exciting times for what promises to remain an active area of basic as well as applied research for decades to come. Returning to Fig. 1, I am waiting, with a bit of mischievous anticipation, to see just where superconductivity will pop up next and force yet another rewriting of our understanding of where it can and cannot exist. ❐

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Acknowledgements

The author's research into superconductivity is supported by the Office of Basic Energy Science, Division of Materials Sciences and Engineering under contract number DE-AC02-07CH11358 and by AFOSR-MURI grant #FA9550-09-1-0603.

Corrected online: 19 April 2011

Correction

In the Commentary 'Still alluring and hard to predict at 100' (P. C. Canfield, *Nature Mater.* **10,** 259–261; 2011), in the second paragraph, the two instances of 'Copper' should have been 'Cooper'. Corrected in the HTML and PDF versions, after print 19 April 2011.