Fishing the Fermi sea

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Sophocles had it right, the Rolling Stones made a friendly amendment and Linus Pauling detailed the conceptual mechanism for finding novel materials that will define and revolutionize the future.

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Figure 1 Humanity realized long ago that skilled fishermen could feed villages and cities. Those skilled in the art of finding the 'right place' to fish were deeply respected and even depicted in art, such as this mosaic at the Archaeological Museum at Sousse, Tunisia.

Within the field of solid-state physics, the discovery of remarkable phases and transitions is often tightly coupled to the design, discovery and growth of novel materials. The past several decades of work in the field of correlated electron physics — that is, the study of materials in which the interactions are sufficiently strong that conventional single-electron theories don't apply — can be described by a list of materials that have defined new extremes, be it extremes of temperature, field, pressure, complexity or, even better, simplicity. In retrospect, it is often clear why, or how, a compound is an excellent example of this or that effect, but one of the nagging questions that is asked at the end of a day, over a beaker of diluted ethanol and/or caffeine, is "where will the next key material be found?" or "what will be the next ________ [fill in your current obsession]?" Often this question seems to be akin to "where will the next bolt of lightning strike?"

In truth, the answer to all of these questions is statistical in nature. Although discovery and 'lightning strikes' cannot be fully controlled, their probability can be enhanced through a series of choices. The design of new materials, at least in bulk crystalline form, is an exercise in trying to improve the odds of finding something interesting. This requires some ideas of how to improve the odds, and some methods of checking whether you have succeeded or not.

To try to design and/or discover a material that will exhibit a specific property, there often needs to be some model or idea of which parameters are important and how to influence or control them. (This guiding principle is often an admixture between theory and practical concerns, such as which elements or compounds can be readily — and safely — used.) For an intermetallic material with magnetic properties, the tendency is to look at compounds with $3d$ transition metals and/or rare-earth ($4f$) elements. To minimize anisotropy, use Gd or divalent Eu (spin $S = 7/2$, angular momentum $L = 0$ moments will have no anisotropy induced by crystalline electric field (CEF) splitting). To study hybridization physics and heavy-fermion compounds (in which entropy is transferred from f-orbitals to conduction electrons, and the interacting electrons can be treated as non-interacting 'heavy' electrons), choose a rare-earth or actinide that is known to be predisposed to interactions between the f and p or d orbitals, which means ambivalent ions such as Ce, Eu, Yb, U or to a lesser extent, Pr, Sm and Tm. For higher-transition-temperature intermetallic superconductivity, try to use light elements and aim for stiff

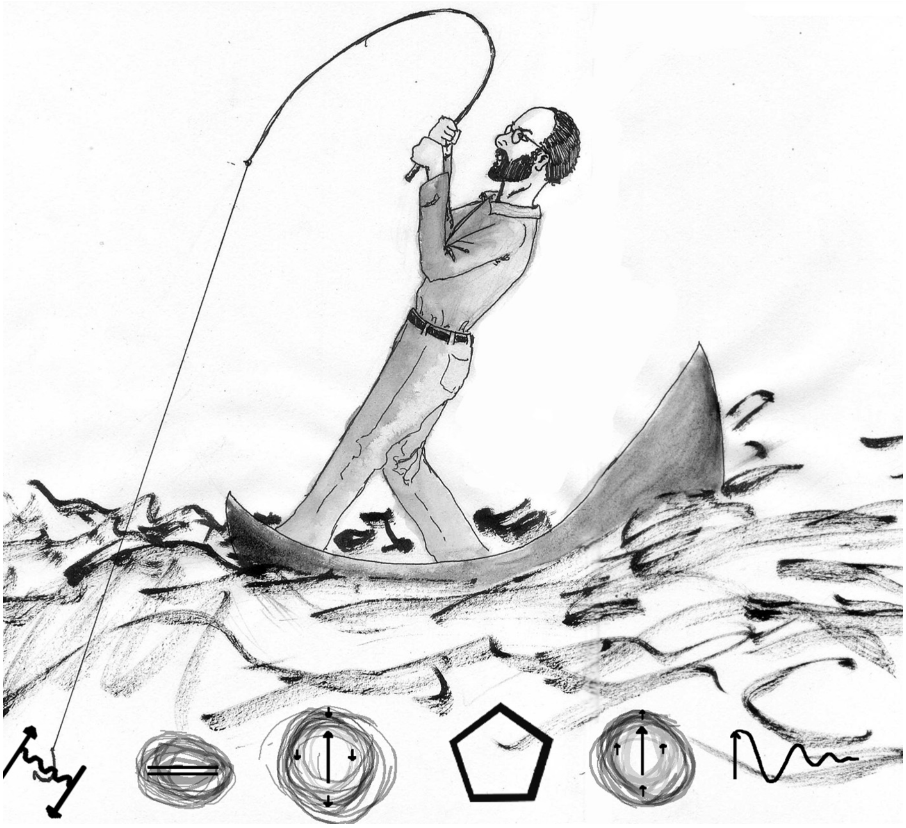

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Figure 2 The scientist who is skilled in the art of new materials design and discovery will develop a variety of strategies for identifying promising spots to fish for new materials and ground states. Those skilled in this art can bring an abundant harvest on novel compounds to the solid-state physics community. Here, the author has hooked a superconductor in a sea that is populated by (from left to right) non-traditional and traditional Kondo systems, quasicrystals, Stoner systems and local-moment magnets.

bonds. In each of these cases, choosing to examine compounds that contain specific elements does not guarantee success (not every intermetallic compound that has a rare-earth and a transition metal is an industrial ferromagnet, not every Ce- or Yb-based intermetallic is a heavy-fermion system), but it does improve the odds of getting what you want. To this end, 'design' is an attempt to use a combination of theory and intuition to shave the dice while playing craps with nature.

Having an idea is the important first step. The equally important second step is having a rapid and efficient sorting measurement that can be used to determine whether the compound indeed has the desired properties. To some extent this process is an experimental realization of a statement attributed to Linus Pauling. When asked how he had so many great ideas, Pauling's answer was, "The way to get good ideas is to get lots of ideas, and throw the bad ones away." For many of the materials and ground-states of interest, a simple thermodynamic or transport measurement (specific heat, magnetization, electrical resistivity) can sort the good from the bad. For example, superconductivity is readily detected in measurements of resistivity, as well as of low-field magnetization.

Having mentioned Pauling, one of the greatest scientific minds of the twentieth century, it is appropriate to recall one of the philosophical observations of some of that century's finest troubadours, Mick Jagger and Keith Richards, who said[1]: "You can't always get what you want, but if you try sometimes you might find you get what you need." When searching for compounds with new or exotic properties this aphorism is very important to remember. It encompasses many examples of what I would call "luck by design", which is best seen and understood by examining some examples from the recent past: $Nd_2Fe_{14}B$ to RNi_2B_2C, to the more recent MgB_2. The first two are examples of accidental addition of an extra element, B and C, respectively.

$Nd_2Fe_{14}B$ is said to have been discovered as the result of trying to make a ferromagnetic binary compound (Nd–Fe) in a BN crucible. According to the apocrypha, some of the B leached into the melt, $Nd_2Fe_{14}B$ formed, and a revolution in high-energy-density ferromagnets began. YNi_2B_2C was originally detected in what was meant to be a ternary, Y–Ni–B, compound. The small amount of C, commonly present as an impurity in B as well as Ni, was enough to stabilize the formation of some YNi_2B_2C, which with a superconducting temperature T_c of ~15 K, was easily detected[2].

More recently, unexpectedly high-temperature superconductivity in MgB_2 was discovered as part of an exploration of the Ti–Mg–B ternary system. In this case, traces of the binary compound were responsible for the superconducting signal, despite the prejudice that such a high T_c could not be found in a binary with only *s* and *p* orbitals[3]. In each of these cases it is to the credit of the discovering groups that they were able to chase the compelling properties they found and identify the compound responsible, despite the differing stoichiometry: they did not get what they wanted, but they did get what they needed.

In each of the examples given above, the discovery was not the result of a random walk through phase space. In each case the research group was searching for materials with specific properties in a phase space that favoured finding such compounds. The fact that they discovered compounds that were unexpected (or even unknown at the time) is certainly not a negative. Sadly, many classically trained physicists are disdainful of such efforts and refer to them as 'fishing trips'. If by this they mean to imply that these groups used random number generators to find these compounds, or threw darts at the periodic table with a blindfold on, then nothing could be further from the truth. In addition, in defence of the term 'fishing trip', a real fisherman goes where the fish are known to congregate and reaps an abundant harvest. A fishing trip provides food for the village. In a similar manner, a scientist trained in the design, discovery and growth of new materials can find materials that create whole new sub-fields, or bring tricky theoretical ideas into crisp and undebatable experimental reality. One has to ask, “What is wrong with this?”

Searching for new materials is not always so unpredictable. Many attempts at design actually work the way they were intended to. To make this as clear as possible, let me review several examples from my own group’s research efforts (simply because I know exactly what the motivations and backstories are in these cases). A clear example of sample design was the discovery of a heavy-fermion ground state in $PrInAg_2$ (ref. 4). The design and discovery of a Pr-based, correlated electron state in this compound involved a cascade of requirements. First we had to have a model to guide our attempt to find the right compound. We assumed that Pr heavy-fermion systems were rare because, unlike Ce and Yb, Pr is a non-Kramer’s ion and in most cases the $R\ln 2$ (or greater) entropy that would be associated with a Kramer’s ion is missing ($R\ln 1 = 0$ for a singlet ground state; R is the gas constant). Thus *a priori* attention needs to be paid to the point symmetry of the Pr ion. In cubic point symmetry a Pr ion can have a doublet ground state, but only over a limited phase space. I started our search by compiling a list of rare-earth intermetallic systems with cubic unit cells. A sub-set of that list contained a single, unique rare-earth site with cubic point symmetry. From this list I chose compounds that did not immediately present profound difficulties (high toxicity, extreme reactivity or volatility).

With this final list (Pr-based compound, cubic unit cell, one unique Pr site with cubic point symmetry) in hand we searched the literature to see if there were data or hints about the CEF-splitting scheme of the compounds. Some were already known to have singlet ground states, and were removed. One, $PrInAg_2$, seemed to have been identified as having a doublet ground state. With all of this planning done ahead of time (design), we synthesized $PrInAg_2$, and on cooling to below 1 K found that this compound was indeed the long-sought, Pr-based heavy-fermion. There was an exceptionally clear separation of energy scales (CEF splitting to the first excited state ~60 K and Kondo temperature ~1 K) and the heavy-fermion state seems to be fundamentally different from Ce- and Yb-based systems in that it is associated with a non-magnetic doublet. It is likely that the transfer of entropy is associated with a dynamic screening of lattice distortions associated with the Jahn–Teller effect.

The search for new systems or ground states can be motivated by schematic rather than detailed ideas or models as well. An example is our recent work on dilute rare-earth-bearing intermetallic compounds: ordered structures that contain less than 5% (atomic) rare earth. We were interested in large-unit-cell materials (as an extension of our earlier work on quasicrystals), and we wanted to push ordered magnetic lattices as close to the single-ion limit as we could (thereby getting the best of both worlds: single-ion-like and yet still periodic). This aim again led, by necessity, to large-unit-cell compounds. By looking at a list of known intermetallic compounds, grouped by unit-cell symmetry and size, and starting from the largest-unit-cell (cubic) compounds, we were able to find a single report of the crystallography of the RT_2Zn_{20} family (R = rare earth and T = transition metal). There is a single R site and the concentration of R is less than 5%. So we went from vague idea to specific, possible compound. As suggested by the stoichiometry, these compounds are actually quite easy to grow as large (cubic-centimetre scale) single crystals out of excess Zn (a low melting element). A few magnetization measurements quickly revealed RT_2Zn_{20} compounds to be very promising, manifesting a plethora of correlated electronic properties associated with both *d*-band and *f*-band physics[5,6].

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Sometimes the search for new materials with specific properties simply involves looking in the obvious places. Whenever we study a rare-earth series, we pay specific attention to the Ce and/or Yb members, examining them as possible heavy-fermion systems. This approach is the solid-state equivalent of ‘rounding up the usual suspects’. When we grew single-crystalline $YbNi_2B_2C$, as part of our study of the RNi_2B_2C magnetic superconductors, we discovered one of the few (at the time) model Yb-based heavy fermions. More recently, when we were studying the RAgGe system, as part of our work on metamagnetism in highly anisotropic, local moment systems, we found YbAgGe to be a rare example of an Yb-based compound that manifests field-induced quantum criticality[7] (the other example, $YbRh_2Si_2$, is discussed in detail elsewhere in this issue[8]). Even though we were studying these families of rare-earth compounds for other reasons, the Yb-based end members often can be interesting in their own right.

Searches for interesting compounds are obviously more successful when the definition of success is allowed to be as broad as possible. This breadth is one of the reasons that groups engaging in such searches often have fairly wide research interests and even wider networks of collaborators. When we find a compound with interesting magnetic properties and which contains iron, we think of Mössbauer spectroscopy. When we find interesting phase transitions in compounds with boron, we think NMR. We have friends who are interested in metal-to-insulator transitions and we have other friends who are eager to look at new examples of layered superconductors. Sometimes realizing that a material is of great interest to somebody other than yourself is almost as important a step as growing the material in the first place.

Regardless of the individual reasons or motivations, it is vital that more people engage in the design, discovery and growth of materials that exhibit new or exotic properties. The more groups that search for interesting and potentially useful materials, the more diverse and viable the ‘idea gene pool’ becomes. Out of these searches, the materials that will be used to address the challenges of the next century will be discovered. On the other hand, if research groups are discouraged from this activity, then it becomes a self-fulfilling prophecy: they will certainly not discover anything. To invoke a final quote, which really sums it all up: Sophocles, in the Theban plays, wrote[9], “Seek and ye shall find. Unsought goes undetected.”

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