Contemporary superconducting materials

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Superconductors currently under active study are briefly described from a chemical perspective. The author's current views on those superconductors, the role of theory in searching for new superconductors, and possibilities for new superconducting materials that might be found in the future are presented.

Introduction

New superconductors are currently being discovered in the world at about the rate of 2 to 4 per year. Although the transition temperature to the zero resistance state is a critical characteristic, other characteristics such as critical current, critical magnetic field, and processability are equally important for possible applications. From a scientific perspective, the underlying cause of superconductivity can often raise forefront issues in condensed matter physics, and has been investigated actively for many materials—ranging from those with T_cs as low as 1 K (*e.g.* Sr_2RuO_4) to those with T_cs above 100 K (*e.g.* the copper oxide superconductors). The search for new superconductors has largely been the domain of condensed matter physicists knowledgeable in the synthesis of intermetallic or oxide compounds. Chemists have much to offer the field, and have also found new superconductors, both in focused searches and by accident in synthetic programs with other goals. Many excellent, detailed reviews of superconductivity and the known superconducting materials are available (see *e.g.* [1–5]). This brief essay is directed at the chemical reader interested in learning about recently discovered superconducting materials, and considering some speculations of mine about the possibilities for new superconductors.

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Recently discovered superconductors

From the chemist's perspective, the most interesting superconductors are those for which many chemical or structural variants can be found. Disappointingly, the superconductors found in recent years have either literally been "one of a kind" or very nearly so. I remain optimistic that new families remain to be found, but it could be that our searches are pushing into the periphery of the stability and chemical and structural complexity for the kinds of relatively simple compounds that can support superconductivity. Some materials of current interest are described in the following.

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Sr_2RuO_4

The magnetic properties of ruthenium-based oxides range from ferromagnetism to antiferromagnetism to Pauli paramagnetism, and the electronic properties range from insulating to metallic. This unusually wide variation comes from the fact that Ru–O networks are poised at the cusp between localized and delocalized electron behavior, with strong Ru–O orbital hybridization. Further, ferromagnetic and antiferromagnetic states at low temperatures are close in energy. The CaO and SrO-based Ruddlesden Popper $(AO)_{n+1}(RuO_2)_n$ series embodies all this complexity in a single family. $Ca_3Ru_2O_7$ is a Mott–Hubbard insulator, $CaRuO_3$ is a paramagnet that can be tipped into ferromagnetism with slight chemical doping, $SrRuO_3$ is a ferromagnet, $Sr_3Ru_2O_7$ is a metamagnet (becomes ferromagnetic, but only under a modest applied field) and Sr_2RuO_4 (Fig. 1) is superconducting at 1 K.[6] There has been a remarkable amount of work on this superconductor in the past decade (see, *e.g.* ref. 7). It looks like the superconducting wave function has *p*-wave symmetry, implying that the superconductivity is a result of a ferromagnetic-like interaction between electrons. Perhaps surprisingly, this 1 K superconductivity has motivated the study and discovery of many new ruthenium oxides. The delicately sensitive superconductivity of this type (a few hundred parts per million impurities are sufficient to kill it—a purity level not commonly achieved in synthesis of complex oxides)

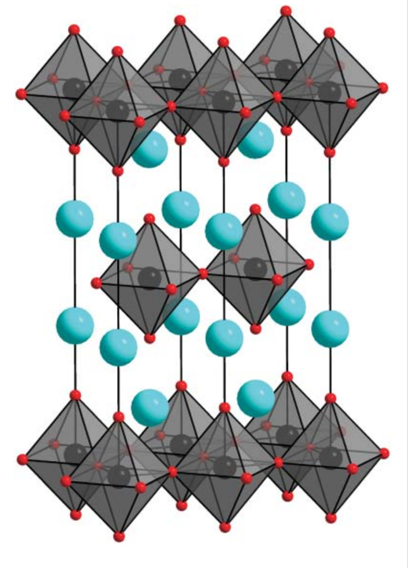

Fig. 1 The layered crystal structure of the 1 K superconductor Sr_2RuO_4. (The Sr are shown as large blue spheres and the RuO_6 octahedra are shown as polyhedra; the Ru are internal to the octahedra and the O are small red spheres). The low temperature superconductivity in this compound is only seen in crystals with unusually high purity and is believed to be unconventional in character. This structure type is commonly found for transition metal oxides, and many studies of two-dimensional conductivity and magnetism have been performed on compounds like this one. The first of the "High T_c superconductors" discovered, $La_{1.85}Ba_{0.15}CuO_4$, has the same basic crystal structure, with some subtle but important differences due to the difference in *d* orbital occupancy.

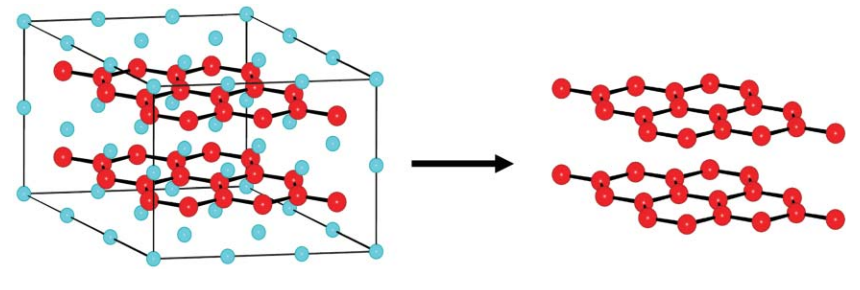

Fig. 2 The layered crystal structure of MgB_2, recently discovered to be superconducting at 39 K, a compound that has been available for purchase from chemical suppliers for many years. (The red spheres are B and the blue spheres are Mg). This structure type, which contains honeycomb layers of boron structurally and electronically analogous to graphite, is found for many transition metal and lanthanide borides. In the case of MgB_2, a critical deviation from full transfer of charge from Mg to B results in the presence of holes in the sigma bonding orbitals of the B honeycomb layer. In contrast, these sigma orbitals are filled in graphite, and superconductivity occurs at lower temperatures when electrons are doped into states that are not as effectively coupled to the lattice vibrations.

has so far made Sr_2RuO_4 one of a kind: superconducting Sr_2RuO_4 can only be obtained in crystals grown by the floating zone method, a method that naturally results in zone-refining of a crystal's impurity content.

MgB_2

MgB_2 is an interesting case, and with a T_c of 39 K[8,9] can be considered the ultimate electron–phonon coupled superconductor. It was discovered to be superconducting in 2001 after being available as a commercial chemical reagent for several decades. This is an example of the surprises in store in this field: who could imagine that a simple binary compound with a T_c of nearly 40 K could lie undiscovered for so long? The diboride superconductors $Nb_{1-x}B_2$ and $(Zr,Mo)B_2$ (with T_cs less than 10 K) have been known since the 1960s, but MgB_2 is special because no *d* orbitals are involved in the electronic system. In the crystal structure (Fig. 2), the boron forms a honeycomb plane, analogous to the C layers in graphite. The magnesium forms a triangular layer between the B layers. If MgB_2 were strictly ionic, then it would be isoelectronic with graphite. Critically, the Mg to B charge transfer is not complete, and the in-plane boron–boron sigma states, which are filled in the case of graphite, are only partly filled in the case of MgB_2, leading to metallic conductivity. The modulation of the in-plane B–B bonds by a phonon therefore strongly impacts the electronic system, and gives rise to the very high T_c. Surprisingly, there appear to be two superconducting systems of electrons in MgB_2—the pi electron states give rise to a lower energy system of superconducting carriers as well! The consequences of this are still under study. Maddeningly, this important superconductor is one of a kind—no additional new superconductors with high T_cs grew from its discovery.

$ZrZn_2$, UGe_2

Magnetic ordering and superconductivity are both cooperative states of electrons at low temperatures, and therefore in some cases can be competitors. For almost all materials, one state is the clear winner, and it is not possible to transform for example from one to another *via* simple chemical or physical means. In recent years fundamental research has been performed on a handful of materials where the two states are very nearly perfectly balanced. From my viewpoint, $ZrZn_2$ is the most interesting of these.[10] It is very weakly ferromagnetic, with a small ordered magnetic moment and a ferromagnetic ordering temperature of 28 K (note that it is made from non-ferromagnetic elements) but also, while ferromagnetic, becomes superconducting at 0.3 K (!). Under a modest applied pressure, both the ferromagnetism and superconductivity go away at the same time, indicating that they are intimately coupled. Related behavior is seen for UGe_2,[11] where ferromagnetism transforms into 1 K superconductivity under applied pressure, though the presence of the magnetic state in the ambient pressure material is less surprising in this case, as U often displays a local magnetic moment. These materials have suggested an interesting new class of superconductors that is likely to have more members—marginally magnetic materials where subtle changes in pressure or temperature tip the balance to marginal superconductivity. These are classic examples of materials that display a "quantum critical point"—materials that display a crossover in physical properties very near zero Kelvin, where quantum effects must rule.[12] Surprisingly, highly unexpected properties are found in such systems at substantially higher temperatures, and these, like other quantum critical materials, are currently of great interest.

$MgCNi_3$

$MgCNi_3$, a new intermetallic perovskite superconductor (T_c = 7 K), has been proposed as another kind of example of a superconductor that derives from a magnet, due to what is believed to be the presence of relatively localized nickel-derived orbitals at the Fermi energy.[13] In this case, a clear link between magnetism and superconductivity has not been found, so it may not be as exotic as originally proposed.

$Na_xCoO_2 \cdot 1.3H_2O$—the devil superconductor

With a T_c of about 4.5 K,[14] this is a wonderful example of an unexpected superconductor found by accident. Due to its fundamentally challenging electronic and magnetic character from a theoretical perspective, I believe this would have been a very important superconductor except that its character as a material precludes it from being studied reliably. The structure (Fig. 3) is based on planes of CoO_6 octahedra fully sharing edges, creating triangular layers. Between these layers is a double layer of H_2O that also contains the Na. At the optimal Na content, the triangular CoO_2 layer contains a mixture of spin ½ and spin zero Co and is electrically conducting. The motion of charge in a layered triangular lattice based on spin ½ is new territory in experimental condensed matter physics, and many strange characteristics are expected and indeed found. The superconducting compound is just barely stable under ambient conditions, decomposing at room temperature at relative humidities of less than 40% (*e.g.* lab air), and at any humidity level for temperatures above 30 °C. I believe that though some reliable papers have been published on this superconductor, there are a larger number of experimental studies that are incorrect. Unless another, chemically stable, superconductor is discovered in this family, the confusion surrounding the characterization of the properties of this material dooms it to a future as muddy as the material itself.

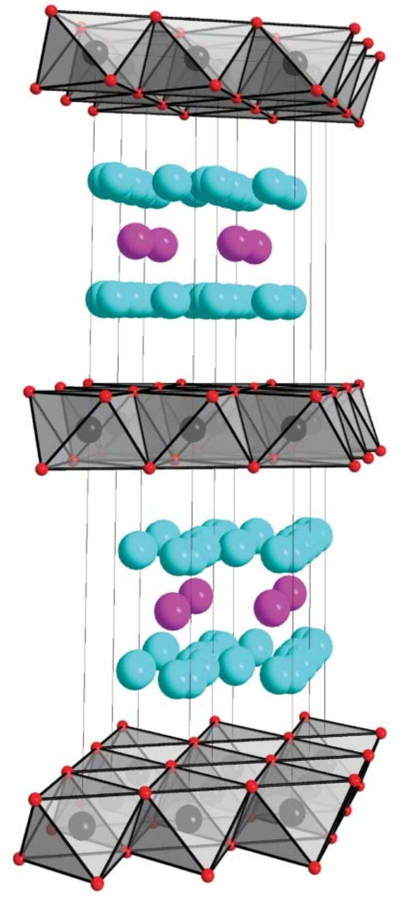

Fig. 3 The layered crystal structure of "$Na_{0.3}CoO_2 \cdot 1.3H_2O$", recently discovered to be superconducting at 4.5 K. (CoO_6 octahedra are shown as polyhedra, the oxygens as small red spheres, the O from the water molecules as large blue spheres, and the Na as purple spheres.) Like Sr_2RuO_4, this superconductor is of interest because there may be a link between the magnetism usually observed in Co-based compounds and its superconductivity. The chemical instability of this compound is at the root of a continuing controversy concerning even its formula: information that is critical for determining the most fundamental of characteristics of the superconductor.

$PuCoGa_5$

This compound was discovered to be superconducting at a very high 18 K, not surprisingly, by materials physicists at Los Alamos.[15] They were investigating the implications of the properties of a similar compound based on Ce rather than Pu, special due to the interactions of localized electrons in the rare earth 4*f* orbitals with delocalized electrons derived from the other metals. When these interactions happen at the Fermi energy, the charge carriers are much heavier than free electrons, by a factor of 1000, and superconductivity can sometimes happen (these are the "heavy fermion" superconductors[16]). This can occur for 5*f* element containing compounds as well, and has been seen previously for uranium. My favorite part of the story is that the disintegrations from the radioactive decay of the Pu cause damage to the crystal structure as the samples age after synthesis. The disorder that this causes in the lattice in turn causes the superconducting transition temperature to decrease over time. However, the increased defect concentration in the compound results in improved trapping of flux vortices in the superconducting state, so at the same time the T_c is decreasing, the superconducting critical current is increasing. Optimal practical properties (though no one would ever market a superconductor based on plutonium!) would therefore hypothetically occur at some finite time after synthesis where the two effects balance.

Pyrochlores

The pyrochlore structure, one of the most commonly found crystal structures in ternary oxides, had not been known to yield a superconductor until very recently. This structure is of substantial interest from a magnetic perspective since the metal sublattices are arranged as corner sharing tetrahedra, a geometry that frustrates the long range magnetic ordering of antiferromagnetically coupled spins at low temperatures.[17] The first of these discovered was $Cd_2Re_2O_7$,[18] and subsequent materials have been osmates like KOs_2O_6.[19] There are enough examples of these that they can now be considered a family, but the fact that they are Os oxides has restricted their study. The evidence so far is that the superconductivity, at temperatures below 10 K, has nothing to do with magnetism or the potential importance of the triangle-based geometry of the lattice.

Elements

In the past decade, the non-superconducting elements have been studied systematically under high pressure to determine whether they can be made superconducting. High pressure decreases the distance between atoms, and orbital overlap is improved dramatically. New solid phases form as molecules break down to form extended solids. Under sufficiently high pressures many nonmetallic elements become metallic conductors, and many have been found to be very impressive superconductors (*e.g.* S at 17 K under a pressure of 2 million atmospheres[20] and oxygen at 0.6 K under 1 million atmospheres of pressure[21]). This kind of experimental work is not for the timid.

Guidance from theory

In my view, one of the joys of solid state chemistry is its unpredictability; both in what kinds of crystal structures form from a particular set of elements, and how to go about trying to make a particular compound by a rational synthetic route. I realize that this is the reason that "real" chemists are wary of us, but most of us have learned to live with that. For my part, I love the fact that there are almost as many ways of looking at the way solid state chemistry works as there are solid state chemists: I am often surprised by the report of a remarkable synthesis or structure that I never imagined would be possible but was obvious to someone else. Trying to design a new compound with a particular set of electronic or magnetic properties is a grand challenge in our field. Given all this, I don't think it is reasonable to ask theorists to be able to predict from first principles what crystal structure a particular combination of elements will form and whether that combination will be superconducting or not.

The prediction of the properties of compounds with known or hypothesized crystal structures is a promising avenue for theoretical support, however. This kind of guidance has taken two forms in the search for new superconducting materials: it has presented general principles for what to try to embody in a material, and also has given recommendations for looking at specific materials. Some of the general theoretical suggestions that I personally have followed up on are: "look for spin ½ systems that you can make into metallic conductors, look for conducting triangular lattices, try to make continuous lattices out of 'valence skippers' (*e.g.* Bi^{3+} and Bi^{5+}), look at materials for which polaronic charge transport is important, look at the boundary between metallic and insulating phases that can be crossed by doping", and others. The physics behind each of these suggestions is quite interesting—spin ½ systems obey quantum mechanical not classical physics, triangular lattices frustrate simple magnetic ordering schemes, valence skipping reflects an intrinsic electronic instability, charge transport by polarons indicates strong electron-lattice coupling, and the crossover point between different electronic states is right where opposing forces come into balance—motivating many studies in the properties of extended solids beyond looking for new superconductors.[22]

Predictions for specific materials are generally based on looking in detail at the properties of a known superconductor and then predicting that a related phase may do equivalently well or better. In my opinion, the most dramatic success of this type of prediction is that the analysis of $BaPb_{0.75}Bi_{0.25}O_3$ led to the suggestion that $(Ba_{1-x}K_x)BiO_3$ would be a better superconductor (it is). The detailed analysis of MgB_2, on the other hand, suggested that isoelectronic LiBC would also be superconducting if successfully chemically doped with electrons (so far, it isn't). There is one interesting aspect of this possible route to superconductivity. Most chemists unluckily do not have the luxury of having a theorist interested in band structures as an available collaborator at their institution. However, there are a few band structure programs now available that are sufficiently "chemist friendly" and accurate enough to be used internally in a synthetic group to help guide which materials to look at most carefully as potential superconductors. There are two ways such programs might be useful: if they predict the presence of a peak in the density of states at or near the Fermi energy at a particular electron count, or if the predicted E *vs.* k dispersion relations show the presence of a Van Hove singularity (a saddle point in the electron energy *vs.* wavevector relations for an electronic band) in the vicinity of E_F. These two criteria are neither necessary nor sufficient to predict that a compound will be superconducting, but they do occur as features of the band structures in many superconducting materials. We have found several examples of such occurrences in the calculated band structures of new materials that unluckily we were not ever able to make superconducting. Obviously, real theorists would have to figure out the potential for coupling these electronic states to the lattice and other important factors to get a real prediction for superconductivity. My guess is that most chemists would not interested in going that far into the theoretical calculations—one might as well just make the compound and test it.

Speculations on the future

It's best not to try to predict the future of new superconducting materials, since we seem to average about one totally new and unexpected superconductor discovered every two years. The best opportunities in well studied materials classes such as the oxides lie in the compounds of marginal stability or syntheses too involved to be attempted by condensed matter physicists. Syntheses of air sensitive materials or at high pressures fall into this category. In intermetallics, it seems to me that the opportunities for finding a new superconductor by conventional synthesis generally lie in quaternary systems, which are largely unexplored. The fact that MgB_2 was missed in the 1960s was due to the fact that it is made with Mg, which requires somewhat more attentive synthetic procedures than were typically used by the people working in the field at the time. In ternary systems, more involved syntheses will still likely bring surprises. My personal view is that concepts such as "valence skipping" have not yet been used to their full advantage in looking for new superconductors, and I think that interesting materials remain to be found in that area. Quite possibly because I don't know enough about it, I think that there must be a goldmine of new organic and molecular superconductors left to find, as many of the known superconductors are chemically and structurally similar. Finally, like many in the field, I think that the links between superconductivity and magnetism are where the richest phenomena and most surprising superconductors likely lie, and that there will be many more like those described above to find in the future. I am an optimist: just when it looks like all the possibilities have been tried, someone will find a new superconductor that will change the direction of the field. The next time that happens you are most welcome to join in. If you are a theorist, I will happily have my students try to make any compound that you suggest might be superconducting as long as it is not radioactive or (very) poisonous. So please send me your suggestions.

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