Materials Design for New Superconductors

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Abstract. Since the announcement in 2011 of the Materials Genome Initiative by the Obama administration, much attention has been given to the subject of materials design to accelerate the discovery of new materials that could have technological implications. Although having its biggest impact for more applied materials like batteries, there is increasing interest in applying these ideas to predict new superconductors. This is obviously a challenge, given that superconductivity is a many body phenomenon, with whole classes of known superconductors lacking a quantitative theory. Given this caveat, various efforts to formulate materials design principles for superconductors are reviewed here, with a focus on surveying the periodic table in an attempt to identify cuprate analogues.

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1. The Materials Genome Initiative

In 2011, the Obama administration announced the Materials Genome Initiative [1]. As quoted that year in a presentation by Cyrus Wadia from the OSTP [2], President Obama stated at the Carnegie Mellon University in June of 2011: *To help businesses discover, develop, and deploy new materials twice as fast, we're launching what we call the Materials Genome Initiative. The invention of silicon circuits and lithium ion batteries made computers and iPods and iPads possible, but it took years to get those technologies from the drawing board to the market place. We can do it faster.* Of course, this did not come out of a vacuum. For a number of years, practitioners of density functional theory had been constructing databases, such as the Materials Project [3], which contains large numbers of electronic structure calculations which could then be data mined for interesting properties. This, combined with high throughput materials synthesis, could indeed accelerate materials discovery [4].

Related to this has been the development of design principles for discovering new materials. For instance, the properties of ferroelectrics are determined by atomic displacements from high symmetry positions. As such, these materials are well suited to density functional methods. As an example, Craig Fennie [5] predicted that a high pressure form of $FeTiO_3$ would be a multiferroic, and this material was subsequently grown by John Mitchell's group and found to be so [6].

Predicting a new ferroelectric is one thing, but a new superconductor is quite a different matter. Even conventional superconductors involve a subtle interplay of electron-ion and electron-electron interactions. As such, predicting even the sign of the net interaction, much less the actual transition temperature, is tough business. Although it took only a few years from the advent of BCS theory [7] to the development of a quantitative strong coupling theory [8], this didn't help us much. The theory did not predict the existence of even the simple material MgB_2 [9], and even after that discovery,

attempts to predict new superconductors based on this class of materials, such as Li_xBC, didn't pan out [10]. Moreover, whole classes of unconventional superconductors, such as rare earth and actinide heavy fermions, cuprates, and iron pnictide and chalcogenides, took the community by complete surprise. One can only imagine what's next.

Still, there have been several interesting attempts to apply both materials genome and materials design principles to the discovery of new superconductors. Here, these are reviewed, with some thoughts about where the field is headed.

2. Materials Genome Ideas Applied to Superconductors

To the author's knowledge, there has been only one 'hit' using materials genome ideas to predict a new superconductor. In 2010, Kolmogorov and collaborators [11] used an evolutionary search procedure to identify new phases in the FeB series. For the several that were found, they then calculated the so-called Eliashberg function, which is the phonon density of states weighted by electron-phonon matrix elements [8]. From this, they predicted that a new orthorhombic FeB_4 phase would have a T_c between 15 and 20K. Several years later, this material was synthesized and found to have a T_c of 2.9K [12, 13]. Although perhaps not the most spectacular success, it does demonstrate that this approach can work. One issue is that even if one has a good representation of the Eliashberg function, the actual value of T_c is suppressed due to Coulomb effects [14]. The calculation of this repulsive $\mu^\star$ is on much less firm ground than the attractive electron-ion interaction, though recent progress has been made [15].

Still, despite materials like MgB_2 with a T_c of 40K [9], T_c of conventional superconductors tends to be limited by retardation effects [16]. The true high temperature superconductors, at least at ambient pressures [17], are cuprates and iron pnictides. Here, we lack even a quantitative theory of what is going on, though most feel that the attractive interaction leading to the formation of Cooper pairs is likely due to magnetic correlations [18]. Still, one could in principle develop descriptors of such materials, and then use them to predict new superconductors.

Perhaps the best known attempt along these lines is that of Klintenberg and Eriksson [19]. Based on a calculation of over 60,000 electronic structures, they then screened these to identify materials with a predicted band structure similar to that of cuprates, that is, a quasi-2D material having a single d-p hybridized band crossing the Fermi energy with a large hole-like Fermi surface around the (π, π) point of the 2D Brillouin zone. Several interesting candidates were identified, such as $Ca_2CuBr_2O_2$, K_2CoF_4 and Sr_2MoO_4. The author is unaware if any of these have panned out. Moreover, there is a fundamental concern with such an approach. Doped layered manganites have a similar Fermi surface as cuprates, as seen by angle resolved photoemission, yet the coherent ground state of this material is ferromagnetism, not superconductivity [20]. This means that the prediction is only as good as the descriptors, or expressed more colorfully, one can easily fall into the GIGO (garbage in - garbage out) mode.

A related attempt has been reported by Curtarolo's group [21], again using structural motifs and band structures as descriptors, but this time looking at a variety of superconducting classes, including cuprates, pnictides, and conventional superconductors. Here, a more systematic approach was employed to identify the appropriate fingerprints within a given class of materials, and then using this to predict T_c. As can be imagined, there were materials whose T_c was bang on, but others where the predicted T_c was way off. To date, if this has led to any new superconductors, the author is unaware of it. Still, this work and the work of Klintenberg and Eriksson is a start, and perhaps with time, will lead somewhere. Certainly, if in the future a 'hit' emerges from these two papers, more researchers will certainly pursue such endeavors.

3. Superconductor Design Principles

The formulating of design principles for superconductors has a long history. Perhaps the most famous advocate for this was Bernd Matthias. His design principles were based on the then known class of highest temperature superconductors, the cubic A15s like Nb_3Sn, and was colorfully summarized in a lecture by Steve Girvin [22]

- High symmetry is best
- Peaks in the density of states are good
- Stay away from oxygen
- Stay away from magnetism
- Stay away from insulators
- Stay away from theorists

This is not completely fair. Bernd was one of the early pioneers of non-conventional superconductors, and in fact advocated looking for uranium-based superconductors proximate to a magnetic phase [23], a prescient hint that eventually led to the discovery by others of unconventional superconductivity in UPt_3 and UBe_{13} [24]. Still, the above design principles, based as they were on the cubic A15 compounds, obviously represented the wrong direction when thinking about materials such as the cuprates, which are quasi-2D doped magnetic oxide insulators. And for sure, Bernd was highly suspicious of theorists, quipping that the development of BCS theory did not lead to any increase in the discovery of new superconductors [25]. On the other hand, the approach is certainly valid in that if the desired design principles are correctly identified, then progress might be made.

Most unconventional superconductors are indeed found in proximity to a magnetic phase. In Fig. 1, the phase diagrams are shown for several classes of superconductors: cuprates, pnictides, 2D-organics, and heavy fermions [30]. In all cases, the phase diagrams are similar, including the not shown example of Cs-doped C_{60} (buckyballs) [31]. One starts with a magnetic phase, typically an antiferromagnet (sometimes insulating, sometimes not), and then uses a control parameter (such as chemical doping or pressure) to suppress the magnetic phase, leading to a superconducting 'dome' that eventually gets
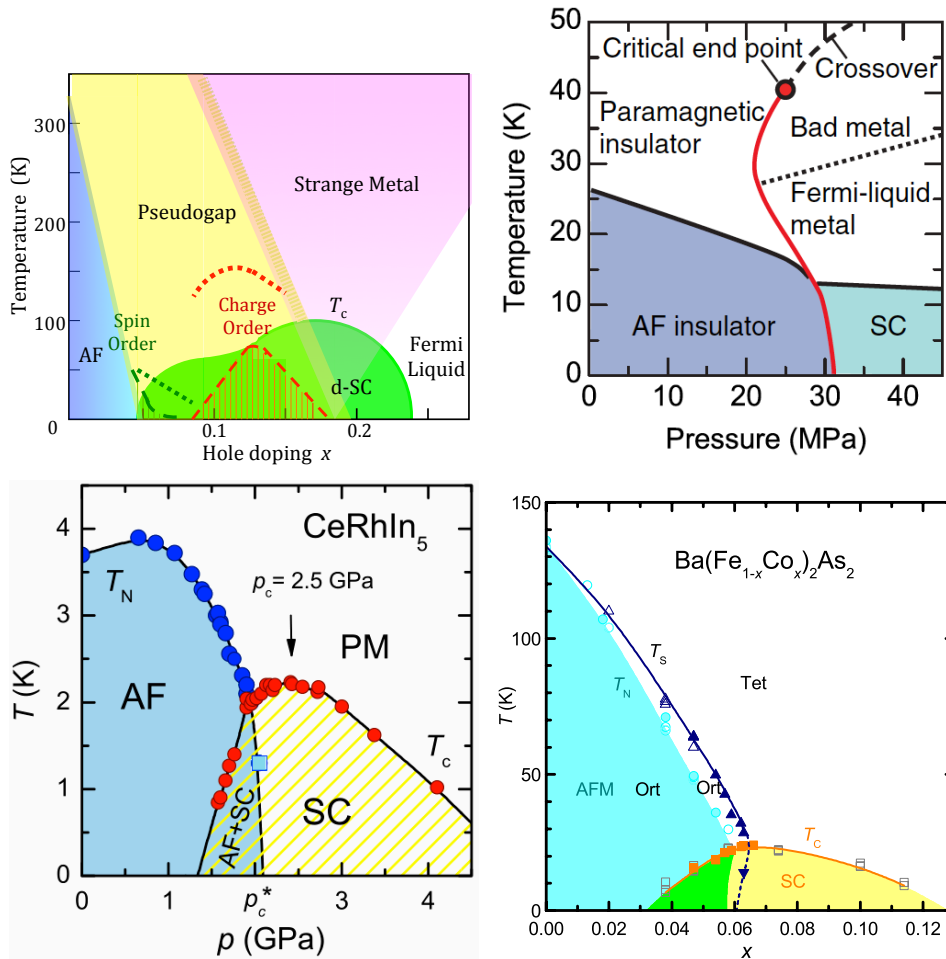
Figure 1. Phase diagrams (temperature versus chemical doping or pressure) for four classes of superconductors: hole-doped cuprates like $YBa_2Cu_3O_{6+x}$ (upper left) [26], κ-$(ET)_2Cu[N(CN)_2]Cl$, a 2D-organic (upper right) [27], heavy fermion $CeRhIn_5$ (lower left) [28], and an iron pnictide, Co-doped $BaFe_2As_2$ (lower right) [29].

suppressed itself as the tuning parameter increases even further. This design principle was realized early on by Gil Lonzarich's group and led to the discovery by them of heavy fermion superconductivity in $CePd_2Si_2$ and $CeIn_3$ [32]. Most recently, it has led to the discovery of superconductivity at high pressures in CrAs [33, 34] and MnP [35, 36], a very unusual occurrence given the strong magnetism exhibited by Cr and Mn. Although T_c of these materials is small (2K and 1K, respectively), a quasi-1D variant, $X_2Cr_3As_3$ (X = K, Rb, Cs) has been discovered with a higher T_c of 6K [37].

This brings us to what I call the Goldilocks principle for high T_c. Quasi-1D superconductors tend to have low T_c since fluctuations kill superconductivity in lower dimensions. On the other hand, 3D materials are limited in T_c because interactions typically are weaker in higher dimensions. So, 2D is just right, and sure enough, the highest T_c materials, cuprates and pnictides, are layered materials.
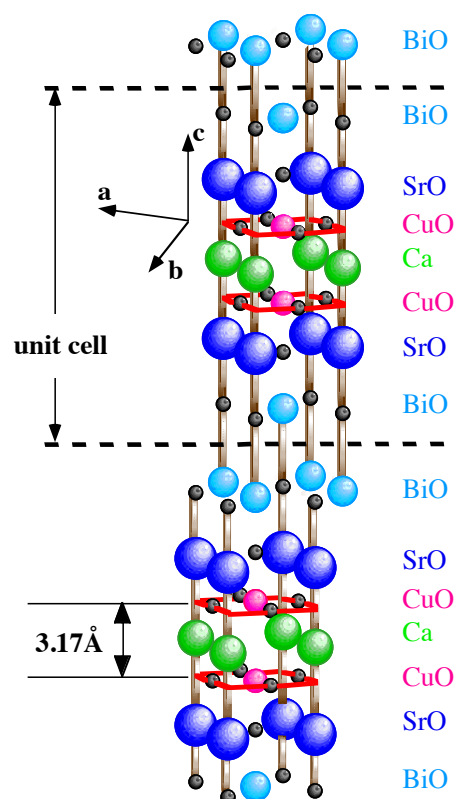
Figure 2. Crystal structure of the cuprate Bi2212 ($Bi_2Sr_2CaCu_2O_8$). Figure courtesy of Adam Kaminski.

We will turn in the rest of this review to surveying the periodic table to see what might be worth exploring, citing relevant work along the way [30].

4. Looking for Cuprate Analogues

4.1. Cuprates

Cuprates [26] consist of CuO_2 layers (Cu being the metal, O the ligand), separated by spacer layers that act to both isolate the active layers, and provide carriers to them to promote superconductivity (the stoichiometric material being a magnetic insulator). This spacer layer is typically composed of rare earths or other metals such as Ca/Sr/Ba, or Hg/Tl/Pb/Bi, either in an isolated form (where they separate CuO_2 layers in bilayer and trilayer variants), or liganded to oxygen (where they separate successive CuO_2 layers or blocks of layers). A good example is Bi2212, shown in Fig. 2. The first thing to realize is the unique Jahn-Teller nature of the Cu^{2+} ion, a design principle that led Bednorz and Muller to the discovery of cuprate superconductivity to begin with [38]. This means that the d^9 configuration of Cu has a single hole in the d x^2-y^2 Kramers doublet. This suggests two possible pictures. In the first, one forms a charge transfer insulator, where doped holes reside in the oxygen orbitals, whereas doped electrons go onto the copper sites [39]. In the doped hole case, the holes on the four oxygen sites surrounding a

copper site form a d x^2-y^2 configuration that reflects that of the 3d hole on the copper ion [40]. In a more traditional band structure approach [41], the nearness in energy of the copper d x^2-y^2 and oxygen 2p states gives rise to a large bonding-antibonding splitting where the d x^2-y^2 state mixes with the oxygen $2p_x$ and $2p_y$ states. The resulting half-filled antibonding band then opens a correlation gap. In both pictures, the Coulomb repulsion plays a fundamental role in creating the insulating state [42]. Carrier doping (for instance, by replacing say a 3+ ion in the spacer layer like La with a 2+ ion like Sr, thus donating holes to the CuO_2 layers) then leads to a superconducting state as shown in Fig. 1. In essence, cuprates can be thought of as doped Mott insulators [43], with the high T_c thought to be due to the extremely large superexchange interaction of 120 meV between the Cu ions mediated by the intervening oxygen ions [42, 43].

Now, how does materials design enter? One of the first attempts along this line was by Ole Andersen's group [44]. They noticed that T_c scaled with the distance, d(Cu-apical O), between the copper and apical oxygen atoms (the copper-planar oxygen separation does not vary much). They realized that the p_z orbital on the apical oxygen, along with the 4s orbital on the copper site, helped to mediate longer range hopping in the CuO_2 planes, in particular an effective hopping integral that acts between planar oxygen ions, denoted as t', with t' and d(Cu-apical O) scaling together. This line of approach has subsequently been taken on by more sophisticated many-body techniques such as dynamical mean field theory (DMFT). Such studies [45] have shown a calculated correlation of T_c with not only these two parameters, but also with the separation of the energies of the d x^2-y^2 and the planar oxygen 2p states (the smaller this energy difference, the higher T_c is). Recently, the same group has used an evolutionary search algorithm to predict new copper oxysulfide variants that could be superconducting [46], an idea that will surely be tested in the near future.

Another approach has been linked to the well known trend for bilayer cuprates to generally have a higher T_c than monolayer cuprates, and trilayer ones to have a higher T_c than bilayer ones (though layer numbers beyond three typically lead to a decreased T_c). The accepted idea is that the electronic structure of the inner and outer CuO_2 layers differ [47], with one set of layers typically being underdoped (and so having stronger correlations) and the other being overdoped (so, more metallic, and thus with a presumably higher phase stiffness that suppresses fluctuations). In general, such composite systems are an ideal way of engineering T_c [48], and sure enough, by tuning the electronic structure of the inner layer by pressure in trilayer Bi2223, one can indeed enhance the T_c of this material to 135K [49].

From the beginning, though, the hope was that by adjusting the metal and/or the ligand ion, one might achieve a new class of cuprate analogues (replacing oxygen by sulfur was already mentioned above [46]). We begin with copper. The superexchange J is largest in materials like those shown in Fig. 2 since the Cu-O-Cu bond angle is 180 degrees, which maximizes this interaction (hybrid density functional based calculations have been able to give a good account of J for a wide range of bond angles involving copper and oxygen [50]). So, you might ask, why would you want to decrease this angle?

The reason is that even if one finds a lower T_c analogue, this might represent a new class of materials. A potential example is the quantum spin liquid Herbertsmithite, $ZnCu_3(OH)_6Cl_2$ [51]. This copper hydroxychloride mineral is composed of buckled $Cu(OH)_2$ layers, with a Cu-O-Cu bond angle near 120 degrees, separated by Zn ions (with Cl ions playing the role of apical oxygens). The important point is that the copper ions sit on a kagome lattice, the most frustrated geometry for magnetism known in two dimensions. In fact, the related triangular lattice was the origin of Anderson's resonating valence bond (RVB) theory [52] which subsequently led to one of the first attempts to formulate a theory for the cuprates [42]. Along this line, Herbertsmithite appears to be a Mott insulator, but does not exhibit magnetism down to the lowest measured temperature [53]. So, what if you could dope it? The success of this is not known (attempts so far have failed [54]), but if you could, then there is a prediction that by replacing Zn^{2+} by Ga^{3+} (which have almost the same ionic radius), one might obtain novel f-wave superconductivity due to the triangular nature of the lattice [55]. If so, then this would be a cuprate analogue to the heavy fermion superconductor UPt_3, thought to be an f-wave superconductor [56] where the uranium ions also sit on a triangular lattice.

4.2. Other 3d elements

We turn now to replacing copper by another transition element. Moving to the left along the periodic table, we first come to nickel. Interestingly, Sr-doped La_2NiO_4 exhibits the same charge stripes as exhibited by underdoped cuprates [57, 58]. But, the material remains an insulator. Unlike the cuprates, where just a few percent of dopants are needed to obtain mobile holes, the doping level in lanthanum nickelate has to exceed 100% doping before a metallic state is achieved. This metallic state looks remarkably like underdoped cuprates, exhibiting a Fermi arc of gapless excitations centered around the Brillouin zone diagonal, but there is no evidence for superconductivity [59]. This might be due to the valence of the nickel (with strontium doping, one is moving from d^8 nickel to d^7 nickel (the cuprates being d^9), or the fact that one is far beyond the doping where superconductivity would have occurred if the doped holes were not localized instead (in cuprates, superconductivity typically only occurs between 5% to 25% doping).

There is, though, one potentially promising direction. A trilayer variant, $La_4Ni_3O_8$, is known that has a crystal structure similar to that of electron-doped cuprates [60]. It is self-doped to 1/3 (hole) doping relative to a d^9 configuration, making this a potential cuprate analogue. This material, though, is an insulator, and was recently discovered to have a similar charge stripe pattern to that exhibited by 1/3 Sr-doped La_2NiO_4, that is $La_{2-x}Sr_xNiO_4$ with x=1/3 [61]. Whether the doping in this 438 material could be altered from x=1/3 has yet to be demonstrated.

Similar physics occurs for the next element over, cobalt, with striped phases existing for Sr-doped La_2CoO_4 over a wide range of doping, analogous to that of the nickelates [62, 58]. Like the underdoped cuprates, an unusual hourglass pattern is seen in the magnetic excitation spectrum (ω versus q), with an intermediate energy magnetic
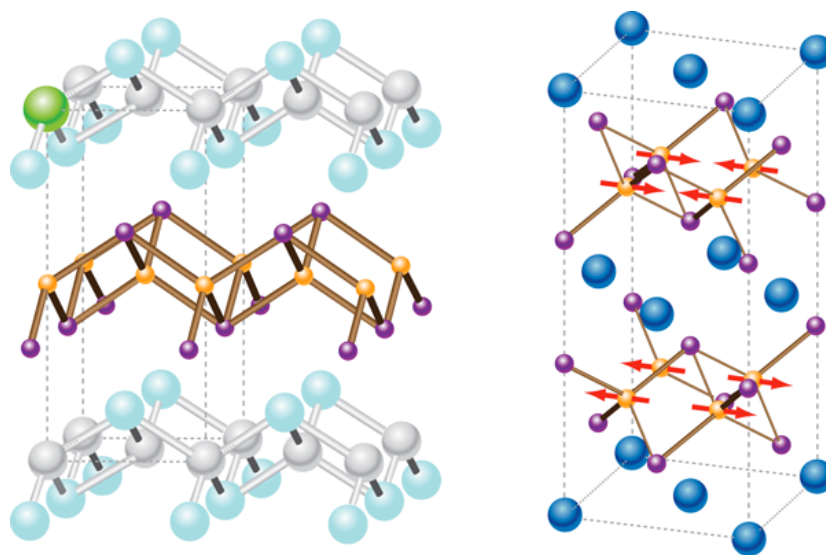
Figure 3. Crystal structures of LaOFeAs (left) [65] and CaFe$_2$As$_2$ (right) [66] denoted as 1111 and 122, respectively. Yellow are iron atoms, purple are arsenic ones. On the left, a fluorine dopant is shown in green. On the right, the spin directions (red arrows) on the Fe sites are shown for the magnetic phase.

'resonance' at $q=(\pi, \pi)$ at the neck of the hourglass [63]. But again, there has been no evidence for superconductivity, with the doped holes staying localized over a wide range of doping. On the other hand, there is a layered cobaltate, $M_x CoO_2$ (with M=Na, K, or Rb, and intercalated by H_2O), where the cobalt ions sit on a triangular lattice, that does exhibit superconductivity at around 5K [64]. The nature of the superconductivity in this material is still an active subject of debate, and whether a variant of this material could exhibit a higher T_c remains to be seen.

This brings us to the next element over, iron. Had Hosono's group stopped after discovering 5K superconductivity in a layered iron phosphide [67], history might have been different. But by playing around with the ligand by replacing P by As, T_c dramatically rose [68], leading to a new 'iron age' for high temperature superconductivity [69]. A variety of crystal structures exist, with the original 1111 material exhibiting superconductivity up to 56K [70]. Other variants are known as 122, 111 and 11, with the 11 variant actually involves S or Te as a ligand (FeSe, FeTe). Two examples (1111 and 122) are shown in Fig. 3. As with the cuprates, these are layered structures, but instead of being planar coordinated like the cuprates, the irons are tetrahedrally coordinated. T_c is very sensitive to the iron-ligand bond angle, exhibiting a sharp maximum when the ligand height above the iron layer is near 1.38 Å [71]. A proper description of these materials is well beyond the scope of this article [72], but again, the phase diagram of these materials is similar to the cuprates (Fig. 1), and the superconductivity is thought to be driven by magnetic interactions [73]. Unlike the cuprates, multiple d-orbitals are involved near the Fermi energy, leading to a multi-band Fermi surface. As a consequence, a sign changing superconducting order parameter (necessary in magnetic mechanisms

where the overall interaction is repulsive [18]) can be achieved by reversing the sign of that on the hole-like Fermi surfaces near Γ relative to that on the electron-like Fermi surfaces at the Brillouin zone boundary [74]. This so-called $s_{\pm}$ state is fundamentally different from the nodal d x^2-y^2 state exhibited by the cuprates, though the true nature of the order parameter is not as clearly known as in the cuprates (depending on the doping and ligand, d-wave and even conventional s-wave states have been advocated as well).

The most popularly studied iron pnictide is the 122 material (XFe_2As_2, with X=Ca, Sr, Ba) which can be doped by substituting on the Fe or As sites. Surprisingly, this $ThCr_2Si_2$ structure is somewhat ubiquitous for superconductors - the original heavy fermion superconductor $CeCu_2Si_2$ [75] exhibits this crystal structure, for instance. Why certain crystal structures seem to be good for superconductivity is still a murky area. A classic example are the UX_3 materials [76]. Most of these have the same cubic A15 structure as mentioned earlier in the context of conventional superconductors, yet are typically vegetables or magnets. But there are two odd ball hexagonal variants, UPd_3 and UPt_3, the former with a dHCP and the latter with an HCP crystal structure. The first has an unusual quadrupolar order [77], the latter is a heavy fermion superconductor [24]. As more such classes of materials are discovered, additional design principles should become apparent [21].

4.3. 4d and 5d elements

Back to the cuprates, what should happen if we move down to the next periodic row instead? The element below copper is silver. One issue with silver is that it typically is a valence skipper, primarily forming either Ag^+ or Ag^{3+}. But under certain conditions it can be stabilized as Ag^{2+}. In that sense, fluorine is a more useful ligand than oxygen [79]. Energetically, the fluorine 2p energies are intermediate between Ag^{2+} and Ag^{3+} as oxygen is between Cu^{2+} and Cu^{3+}, leading to similar charge transfer physics [80]. The big problem is getting these fluoroargentates to form the desired layered structure [80]. One issue is that Ag^{2+} often exhibits an inverse Jahn-Teller configuration (with the d^9 hole in the $3z^2$-r^2 orbital instead), and even if found in a Jahn-Teller configuration, it often responds by forming AgF_4 units whose normals are not along the *c*-axis (Fig. 4) [81]. Finding the optimal 'cuprate' configuration (flat AgF_2 sheets with a long apical axis parallel to *c*) is a difficult challenge that has yet to be realized [80]. In that context, a recent set of density functional calculations were done to predict superlattices that would stabilize such a structure [82]. Although synthesizing these materials could prove to be difficult, a success here could start a whole new field of superconductivity [83]. Now, there are oxides of silver which are low T_c superconductors, such as $Ag_7O_8HF_2$ [84], but these clathrates' superconductivity likely originates from 'rattling' modes of HF_2 centered in the large Ag_6O_8 cages of this material.

The next element over in the 4d row is palladium. As with nickelates, Pd^{2+} is d^8 rather than d^9 and so is expected to differ from cuprates. On the other hand, Pd
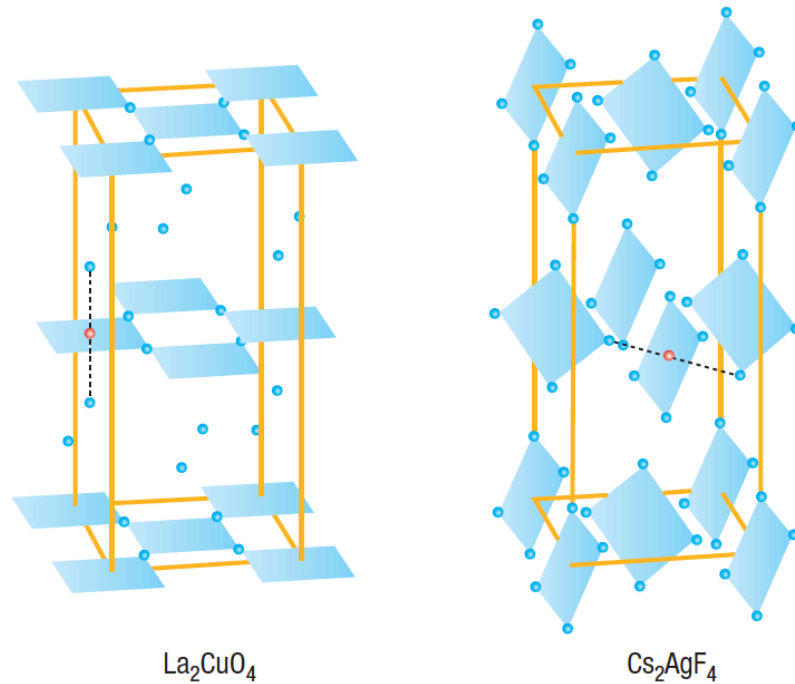
Figure 4. Comparison of crystal structures of La_2CuO_4 (left) and Cs_2AgF_4 (right) [78]. The shaded squares represent CuO_4 and AgF_4 plaquettes, with the apical axis shown as a dashed line.

metal is nearly ferromagnetic, and so Pd compounds can be expected to have interesting magnetic properties. And if the magnetism is suppressed, who knows, perhaps some kind of superconductivity might be observed. The prediction of p-wave superconductivity in Pd goes back a long time [85], and though not realized (yet), was shortly thereafter co-opted to be one of the leading theories for triplet superfluidity in ^{3}He. In that context, the recent observation of ferromagnetism in $Ba_2PdO_2Cl_2$ is of note, this material having a similar crystal structure to that of electron-doped cuprates [86], so doping studies could be of interest. In connection with the iron pnictides, superconductivity at 3.9K was recently discovered in $BaPd_2As_2$, possessing the same $ThCr_2Si_2$ crystal structure as $BaFe_2As_2$ [87].

No further remarks will be made about the 4d row, expect to note that low temperature, probably p-wave, superconductivity has been found in Sr_2RuO_4 [88], with its bilayer variant, $Sr_3Ru_2O_7$ [89], exhibiting electronic nematic order as also seen in the cuprates and iron pnictides.

We now jump down to the very interesting 5d row. Although a variety of Pt and Au compounds have similar formula units to their cuprate counterparts, the discussion here is confined to two 5d elements, Os and Ir. Os is interesting in that it exhibits a variety of valence states, and so there is a vast materials space here remaining to be explored. A magnetically frustrated pyrochlore, KOs_2O_6, exhibits low temperature superconductivity, but this is likely due to K 'rattling' modes, making the material
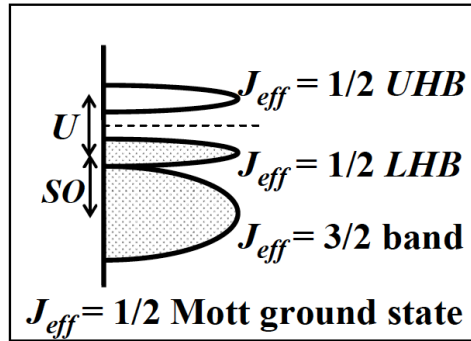
Figure 5. Electronic structure of Sr_2IrO_4 [91]. U is the on-site Coulomb repulsion, SO the spin-orbit splitting, with LHB and UHB denoting the lower and upper Hubbard bands. The dashed line is the chemical potential.

similar to the AgO clathrate that was mentioned earlier [90].

Of perhaps greater interest is iridium. Sr_2IrO_4 exhibits a similar electronic structure to cuprates despite its d^5 configuration (Fig. 5). This is due to the profound effect of spin-orbit, which splits the t_{2g} manifold into a filled quartet and a half-filled doublet [91]. Although there are definite differences (the iridates are likely not charge transfer insulators due to the smallness of the Hubbard U and the energetic separation of the Ir 5d and O 2p states), still, the presence of a half-filled Kramers doublet that opens up a correlation gap is reminiscent of the cuprates (and the stoichiometric material is an antiferromagnetic insulator as well, just like the cuprates). This has led to the prediction of unconventional superconductivity [92]. Unfortunately, iridates, having Sr in its spacer layer rather than La, have proven to be difficult to chemically dope. On the other hand, surface sensitive studies have made some progress along these lines. By depositing potassium on the surface to dope it (a 'trick' that was earlier used for cuprates [93]), B J Kim and collaborators were able to observe Fermi arcs in iridates, very similar to what was seen in underdoped cuprates [94]. More recently, by introducing bilayer inclusions (which are metallic), they have been able to exploit their screening to go to low temperatures and observe a d-wave energy gap [95] that has also been seen by STM [96]. This leads to the hope that an appropriately doped sample might exhibit superconductivity.

This brings us to an important point. Although much theoretical work has been devoted to ideal materials, there has been much less attention given to doping. This is obviously an issue, since most of the interesting materials like cuprates, pnictides, and buckyballs, are rarely superconducting in their stoichiometric phases, and require some form of chemical doping to achieve superconductivity. Many interesting stoichiometric materials, like the above example of iridates, have proven difficult to dope. And others, once doped, often exhibit charge localization (nickelates and cobaltates being relevant examples). Earlier, the interesting case of Herbertsmithite was mentioned, which was predicted in its doped state to be a novel superconductor [55]. Recently, a density functional study was done to investigate doping 3+ and 1+ ions on the Zn^{2+} interlayer

sites, with the claim that a number of such ions are promising candidates [97]. On the other hand, synthetic techniques have so far failed [54], likely due to the fact that in reality, these copper hydroxychloride minerals can only accommodate 2+ ions on the interlayer sites (otherwise, they fall apart). Therefore, much more challenging work remains to be done, both experimentally and theoretically, before we get a handle on the crucial issue of chemical doping.

5. Exploiting Layering

The above mentioned superconductors are not the only layered ones. There is a class of layered nitrates that have T_c up to 26K, HfNCl and its siblings (ZrNCl, TiNCl) [98, 99]. These are ionic band insulators, and although the electron-ion interaction is likely prevalent, other interactions also come into play [100]. Doping is achieved by intercalation (such as with Li), but so far, only electron doped materials have been studied (with the doped electrons entering the empty d bands). Hole doping, where the doped holes enter into the ligand 2p states (as in the charge transfer picture for cuprates), would be interesting. In that context, the stoichiometric material has also been made superconducting by liquid ion gating [101], and so one could easily reverse the gating potential and see what happens.

This brings us to a vast new field where in this short article, justice cannot be given. This is the study of engineered 2D materials. This takes two forms. First, superlattices of materials can be constructed by MBE growth. There have been a number of successes here. In cuprates, one can take blocks of material which are respectively undoped insulators and heavily overdoped non-superconducting metals, and then at their interface, high temperature superconductivity can be achieved [102]. Or, one can take a single layer on a substrate and gate it as mentioned in the previous paragraph, leading to superconductivity in a variety of 2D materials [103]. Perhaps the most spectacular example is the recent claim of superconductivity near 100K in a single layer of FeSe on top of a substrate [104].

Related to this has been the development of a new modular design principle that treats layers (or multilayers) much like Lego blocks that can be interchanged to engineer new materials. Several years ago, this was used to predict the existence of a complex iron oxide phase, $Y_{2.24}Ba_{2.28}Ca_{3.48}Fe_{7.44}Cu_{0.56}O_{21}$, related to that of Bi2212 [105]. The synthesized structure was close to the predicted one. More generally, most oxides are octahedrally coordinated, and given their importance for a variety of desired physical properties (ferroelectricity, magnetism, etc.), design rules have been developed known as 'octahedral engineering' [106]. The impact of both of these works on superconductivity could be realized in the near future.

6. Some Final Thoughts

Just because one has discovered a high temperature superconductor does not mean that technologically, it would have any relevance. A trivial example is the recent spectacular discovery of ultra-high temperature superconductivity (near 200K) in H_3S under extremely high pressures [17]. Such high pressures are needed to metalize the hydrogen (sulfur acting as a matrix to help bring the needed pressure down), with the prediction that metallic hydrogen would be superconducting due to its high energy phonon modes being made a long time ago [107]. But a more relevant example are the layered materials we have been focusing on in this review. In two dimensions, a true superconducting transition does not exist, rather one gets a Kosterlitz-Thouless transition [108]. 3D coupling between the layers stabilizes 3D superconductivity, but as this coupling is weak, it has a weak effect on pinning vortices. So, the combined effect of fluctuations (always relevant below 3D) and weak pinning is detrimental for obtaining high critical currents [109]. This is one of the reasons that cuprates have made a small impact so far on technology despite their high critical temperatures. Recent progress has been made, though, on designing pinning landscapes to optimize superconductors, both for cuprates and for iron pnictides, leading to a 'materials genome' for defect engineering in superconductors [110]. That is, designing superconductors requires not only tuning the electronic structure and interactions (via the choice of metal, ligand, and crystal structure), but also by tuning the carrier concentration (chemical doping or pressure) and the defect landscape (to enhance pinning). It is only by thinking about all three of these facets will we have a hope of designing ideal superconductors.

I end, though, with a cautionary note. The history of superconductivity has been littered by bad ideas. Perhaps the most colorful description of this has been given by Bernd Matthias in a number of talks, that although over forty years ago now, still seem highly relevant today:

- *The electron-phonon interaction always reminds me of the man who is looking for his keys under a street light and his friends say "but you didn't lose them here, you lost your keys over there". "I know, but it is too dark over there."* [111]

- *Sometimes this thing reminds me of the Virginia Wolf play where four people argue all night about the aberrations of a child, and when the play is over, it turns out that there never was a child. This is exactly how I feel about the organic superconductors.* [111]

- *That of course leads you to Green's functions and the absence of any further predictions.* [112]

- *Unless we accept this fact and submit to a dose of reality, honest and not so honest speculations will persist until all that is left in this field will be these scientific opium addicts, dreaming and reading one another's absurdities in a blue haze.* [113]

Who knows, perhaps he would have had bad thoughts about a 'material genome' approach to superconductivity as well. Certainly, there is a lot of skepticism in the field

about reliable predictions concerning superconductivity based on electronic structure simulations [114]. After all, almost all of the great discoveries in the field have been made serendipitously [115]. Still, until such predictions can be made, then we will not truly understand the phenomenon of superconductivity in its many varied forms. This is indeed a noble goal to strive towards.

Acknowledgments

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