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Orbital-selective hole and hole-pair formation and Bose Condensation in high-temperature superconductors

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Abstract

Miguel Alario-Franco is recognised not only for his seminal experimental advances in the field of High T_c superconductivity but also for his incisive observations on the advances – and the challenges - in the field. In 1995, he highlighted the need for "a new theme" to unite the chemistry and the physics of this spectacular natural phenomenon following the advance by Bednorz and Muller, that surely ranking as one of the greatest-ever discoveries in science.

We review the remarkable recent advances that showed hole (and electron) pairing in the cuprates is found at temperatures above Tc. Hole-pairing above T_c was first proposed over 3 decades ago by Mott and Alexandrov. We highlight that the pairing itself will be 'orbital -selective'; holes of predominantly one specific orbital character bind to form the Cooper pairs which then yield the High T_c state.

Here, a collection of friends and colleagues of Miguel from the disciplines of chemistry, physics, and electronic engineering outline how this as a working, chemically intuitive model in the search for other High T_c materials.

Prologue

Miguel has noted that dedicated solid state chemists will always continue their search for other (hopefully, better) High T_c superconductors even in the absence of any universally-accepted theory of the phenomenon but guided as Roald Hoffmann noted - by "chemical intuition" in its most powerful form [1]. In 1995, in an insightful essay, our 'Birthday Colleague' presented an important overview [2] of the advances made in the eight years that had elapsed since Bednorz and Muller's epoch-making discovery of High Temperature Superconductivity (HTS) in the layered cuprates [3] With that discovery, there was real hope and anticipation for the emergence of an accepted theory for this spectacular phenomenon and the discovery of new classes of materials superconducting at temperatures above liquid nitrogen. Unfortunately, no such universally accepted theory has emerged.

Miguel's assessment was that "Chemical ingenuity, once again, has greatly improved the HTS materials". Hopefully, an example from our own work [4, 5] of such an improvement through the 'Chemical control of HTS', might be taken as a positive reflection of such advances (Figure 1).

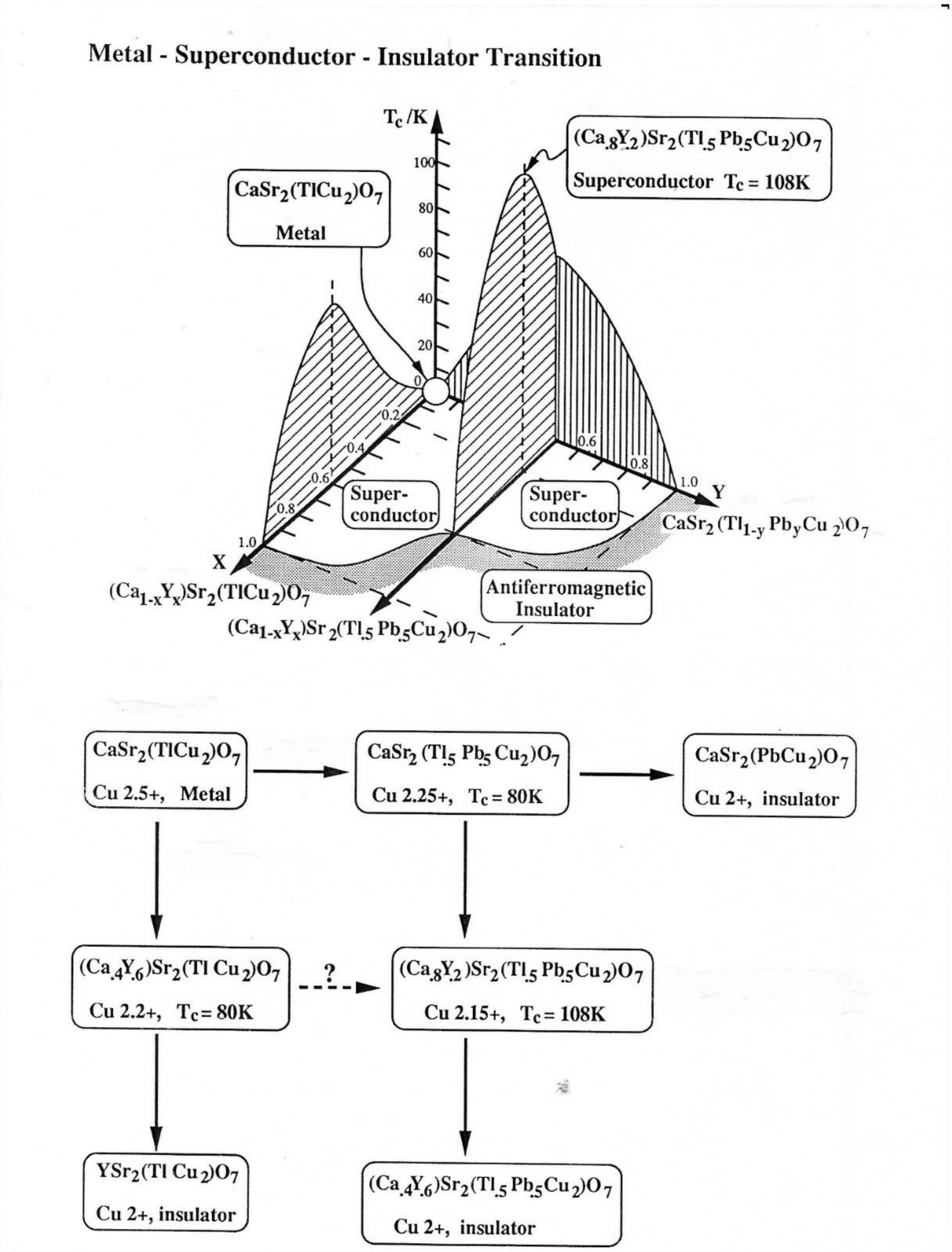


Figure 1. The chemical control of High Temperature Superconductivity in the septenary cuprates [4]**; illustrated from the original data by W Y Liang (Cambridge University)**

The cuprates are the only materials at room pressure that have superconducting transition temperatures, Tc, well above the boiling point of liquid nitrogen [6]. However, whilst there are a large number of chemical variants, as exemplified in the septenary cuprates, once the materials are discovered, the chemical control of HTS is powerful and extant. Importantly, the cuprate superconductors all derive from a common, characteristic layered structure made up of one or more CuO_2 planes with intervening charge reservoirs (Figure 2).

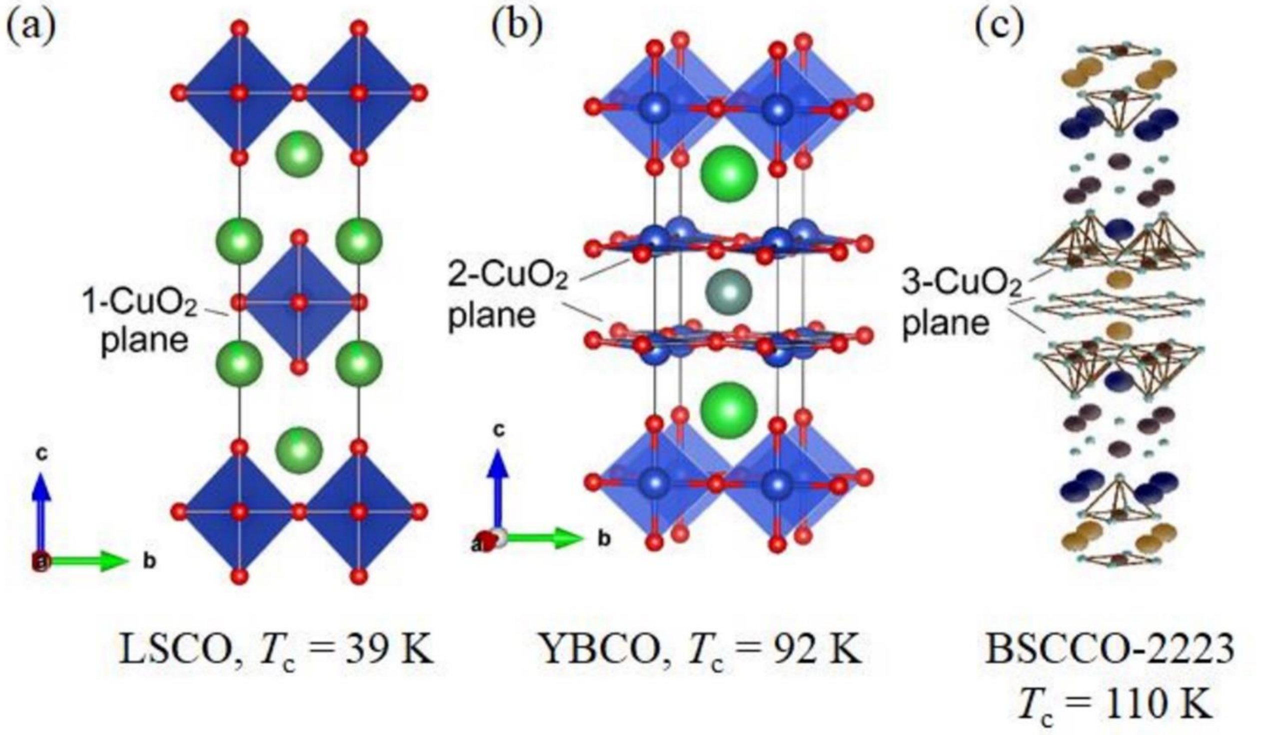


Figure 2. The crystal structures of the High Temperature Superconducting Cuprate family. [7]

Miguel correctly argued that in both structural and compositional terms, despite impressive advances in HTS in the layered cuprates, we have - adopting a musical paraphrase - simply been relying upon "...variations on an original theme"[2]. Thus, the vast majority of materials have superconductivity residing in CuO_2 layers supported by a perovskite skeleton, and supplied with excess holes or electrons by the intervening charge reservoir layers

With that in mind, Miguel concluded - with a characteristic incisive and almost plaintive statement - "Yet, if a new theme could be found…".

This, then, is Miguel's potent challenge for us all … that of … "finding a new theme" in understanding HTS and helping to look for other such materials across the Periodic Table. After 35+ years of intense effort, a universally-accepted microscopic theory of HTS is still not established, and that is clearly hampering further progress. It appears, for example, that the cuprate and iron-based superconductors are not amenable to standard ab-initio tools due to strong electron correlations and their proximity to magnetism.

Whilst being conscious of the strong assertion by P.W. Anderson [8] that "...The consensus [*on an accepted theory of High Tc*] is that there is absolutely no consensus "we attempt to present here a brief overview of recent important developments which may provide a new theme or new themes for a mechanism for HTS, leading to the discovery of other superconducting materials with, potentially, even higher transition temperatures.

We focus on the microscopic origins of the critical hole - formation and hole-pairing mechanism of Cooper pair formation in the cuprates and iron-based superconductors in terms of a highly specific orbital-selective hole formation and hole-pairing. We then discuss the ensuing composition-induced insulator-to-strange- metal transition and, finally, the vexing question of the striking rarity of High Tc in materials across the Periodic Table.

Cooper pairs and the insulator-to-strange metal transition in the layered cuprates

The phenomenon – and explanation – of HTS in the cuprates must surely be embedded in the chemistry and physics of the copper-oxygen layers, suitably 'tuned' either by chemical (substitutional) doping or through auto-injection of charge into the CuO_2 layers (Figure 2).

Most notable of all developments since Miguel's essay has surely been the widespread realisation *and* identification in the HTS cuprates of the existence of preformed pairs of charge carriers – Cooper pairs – *existing above Tc*, not only giving rise to HTS but also a 'strange metallic state' in the normal state itself [9-12]. In conventional superconductors, Cooper pairs are assumed to form *only at Tc*, where macroscopic coherence of the pairs occurs and superconductivity sets in. In contrast, for the cuprates , it is now acknowledged that Cooper pairs form well above Tc and become coherently mobile and condense to the superconducting state when the material is cooled to the critical superconducting temperature.

One can readily see as to why the growing appellation of 'strange metals' [13, 14] is so readily applied to the cuprates at T > Tc by looking at a generic material-sorting - map (Figure 3) involving the electron (hole) densities and electron (hole) mobilities of three prototypical cuprate materials in their normal state as compared to other conducting oxides as well as 'Good' and 'Bad' elemental metals (non-superconducting and superconducting metals, respectively),

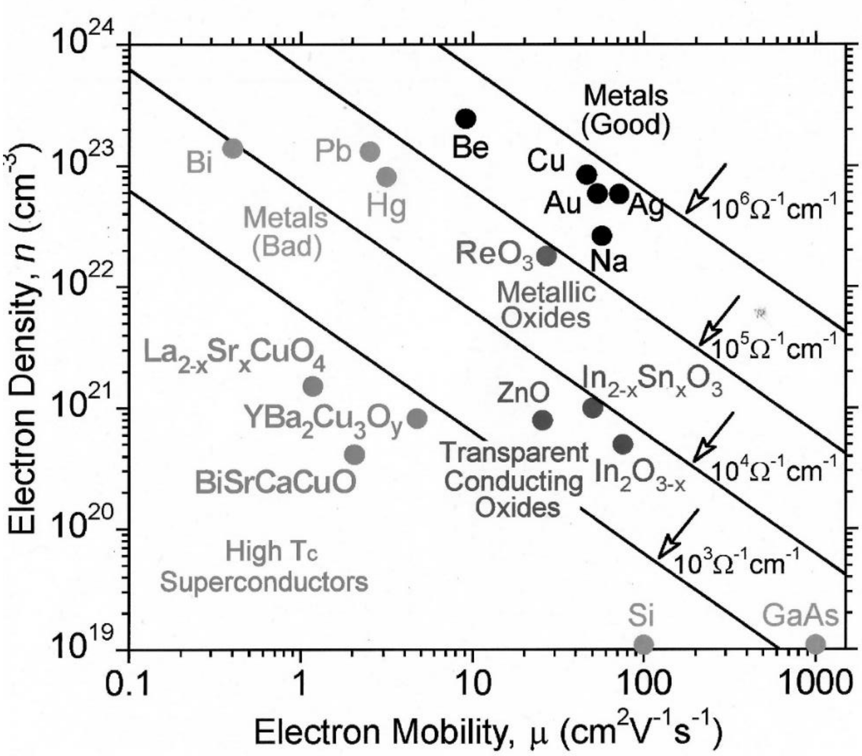


Figure 3. A Materials Sorting Map (modified from [15]) to include High Tc Superconductors. Modifications courtesy of Dr V. L Kuznetsov (Oxford University)

The consensus now emerging is that even in the normal state of HTS cuprates, Cooper pairs, or bipolarons, acting as bosons, are the carriers of electrical charge, unlike conventional metals where single electrons fulfil that role. In these cuprate materials – and potentially other superconducting materials – we see the emergence of a new type of 'strange metal' in which in their normal states, a significant fraction of the electrical current is carried by mobile electron pairs [10, 13, 14, 16, 17]. Indeed, that scenario was first advanced in the 1990's by Mott and Alexandrov [18-22] and elaborated upon by Edwards, Mott and Alexandrov [23].

A recognised and common feature is that the HTS cuprates are strongly correlated electron systems and magnetism and superconductivity either co-exist or are nearby in their phase diagram (Figure 4).

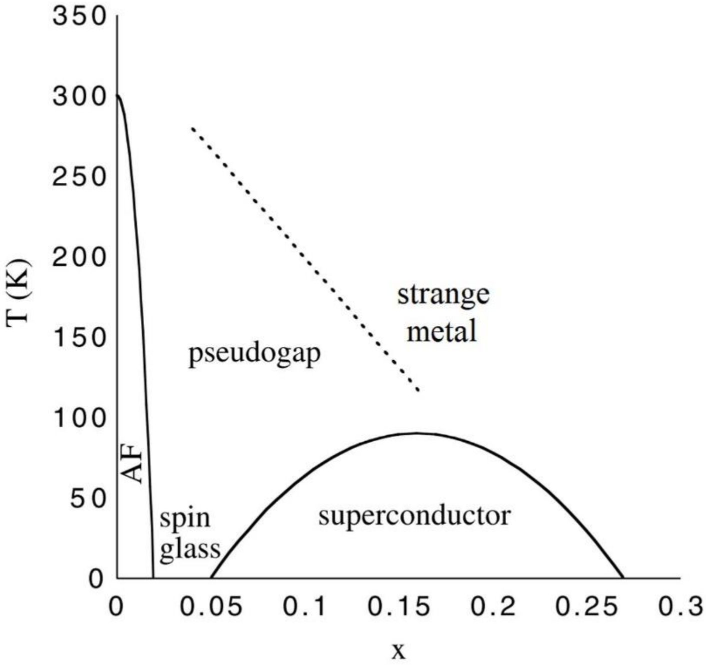


Figure 4. Schematic phase diagram for the layered High Tc cuprates (modified from ref. [24])

This observation has been taken as a strong indication that spin fluctuations are a key ingredient in the mechanism for superconductivity. HTS in the cuprates emerges from magnetism upon hole doping of the parent antiferromagnet, La2CuO4. The existence of a 'parent' Mott insulator, e.g. in the prototypical cuprate, La_2CuO_4, being a spin 1/2 antiferromagnet, has led to the generally-accepted view that the high Tc cuprate superconductors can be viewed as a class of doped semiconductors with electronic properties on the insulating side of any transition to the metallic and/ or superconducting state, being qualitatively similar to that in conventional semiconductors.

At zero hole -doping, particles are localised by strong Coulomb repulsions (the Hubbard U) and order antiferromagnetically (**Figure 4**). By substituting trivalent La for divalent Sr in $La_{2-x}Sr_xCuO_4$, x "excess" holes are added to the two-dimensional CuO_2 layer with their concentration dictated by the compositional parameter, x. Thus, the composition-dependent, in-plane CuO_2 electronic structure and properties are dominated by holes, introduced randomly by chemical doping (e.g. substitution of Sr_{2+} for La_{3+} in $La_{2-x}Sr_xCuO_4$). Such structural and electronic disorder gives rise to a mobility edge in the electronic density of states in this 2D system

With increasing x, as holes are continuously added, the low temperature antiferromagnetism (AFM) disappears and – ultimately- an unconventional, strange metallic state emerges in the normal state and High Tc at lower temperatures. Many authors have proposed that this characteristic magnetic behaviour – strong antiferromagnetism within the 2D CuO2 planes (Figure 2) being modified by added holes - might provide the gateway to HTS. Here, the magnetic 'glue' responsible for hole-Cooper pairing and HTS coming from dynamic spin fluctuations associated with proximity to an antiferromagnetic state.

Jarrell *et al*. and others [25, 26], early on, outlined a phenomenological model for the composition-induced insulator-metal transition in the cuprates in which the electronic conduction is shown to be predominantly intralayer, i.e. confined to the Cu-O layers. In the parent compound La_2CuO_4, the formal valence of Cu is 2+, which means its electronic configuration is d^9. The local crystal symmetry splits the constituent, e.g. orbitals, so that the highest partially occupied d-orbital has the character $d_{x^2-y^2}$ (Supplementary Information).

At low doping (substitutional) levels, the excess hole (acceptor) states occupies a two-dimensional hydrogenic orbital in the CuO_2 plane. The oxygen holes are at first localised/coulombically bound to their accompanying (parent) dopant ion (e.g. Sr^{2+}) and have a characteristic Bohr radius of between 8+/- 2Å in the CuO_2 plane, typically encompassing 1-2 unit cells. The temperature dependence of the electrical resistivity in the insulating regime in the cuprates has been attributed to variable-range hole hopping of excess charge carriers between Anderson- localised states [25, 26].

At higher values of x, as charted by Catlow, Islam and co-workers [27-30], we see the natural progression to the formation of bound hole pairs, (peroxy) bipolarons, also spatially localised at these intermediate values of the compositional parameter x.

Importantly, hole formation and the subsequent hole- pairing itself appears to be orbital – selective, meaning that excess holes and pairs of holes are formed from specific atomic orbitals of the oxidised O2- ion to yield O.- and these states ultimately combine to form the Cooper pairs of the superconductor.

Catlow, Islam and co-workers have investigated in detail the atomic/orbital structure and energies of such bipolarons in substitutionally- doped La_2CuO_4 [27-30].

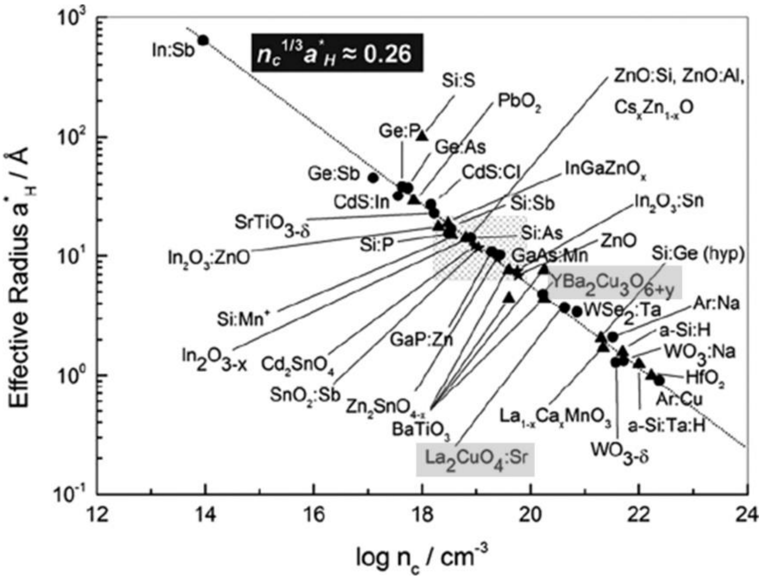


Figure 5. A plot of the critical carrier density, n_c, as a function of a_H*, the effective Bohr orbit radius of a range of materials (Ref [31]). The conditions for the metal-insulator transition for two cuprates are shown in grey shading.

Now, once formed, these charged spin-zero bosons, like ordinary single electron/hole carriers in doped semiconductors, screen the random, localising potential. As noted by Alexandrov and Mott [21] it is expected that the Mott criterion for the insulator-metal transition [32] will be valid also in the case of Bose particles, with 2n instead of n and aH* = ...and with ε0 ~ 100 and m* ~ 10me this yields a critical density (nc) for the metal-insulator transition of ca. 10v21 cm^{-3} (Figure 5).

The generally- accepted phase diagram in the cuprates shows the consequences of adding "excess holes" to the CuO2 planes through chemical substitution and the evolution, ultimately, to an anomalous or strange metallic state from a Cooper-pair insulating state separated at the lowest temperature by a Quantum Critical Point, QCP (Figure 4).

Of course, the high- and low - temperature (T = 0K) crossover behaviour from insulator- to – (strange) metal is completely hidden under normal conditions by the existence of the high-temperature superconducting phase.

Applying a high magnetic field to suppress superconductivity enables a detailed study of that electronic transition in the normal state. Boebinger *et al*. [33] were first able to study the basic insulator-metal transition, in the absence of superconductivity, as a function of carrier concentration achieved by using a 61T pulsed magnetic field to suppress superconductivity in $La_{2-x}Sr_xCuO_4$ single crystals.

The remarkable finding is that the insulator-to-metal crossover transition occurs for compositions near optimum doping. Thus, the low temperature (normal state) insulator- (*now*) strange metal transition, reflected in the modified Mott criterion, where the carriers are bosons rather than fermions, is linked to the carrier concentration at the optimum Tc of the superconducting phase of the layered cuprate. This reflects the condition for the Bose-Einstein Condensation of the doubly charged, paired-hole carriers, or bipolarons, into the superconducting state of the layered cuprates [23, 34].

Mott first proposed [18, 19] that this non-degenerate gas of bosons carries the current above Tc and accounts for the abnormal behaviour of this strange metal not shown by conventional BCS-type superconductors in their normal state.

It is also now recognised that when electrons (or holes) form Cooper pairs in a 2D disordered system (such as the cuprates (Figure 2)) the ground state must *either* be a superconductor *or* an insulator with, interestingly, *no intervening, conventional "metallic state"* [23]. This is recognised from the scaling theory of localisation, which predicts that a conventional metallic state is absent at T = 0K in such disordered systems because of quantum interference [35, 36].

We now turn to the specific orbital structure at a microscopic level upon the introduction of excess holes in the CuO_2 layers and how they interact to form hole-pair bosons which then carry the supercurrent. We highlight how orbital structure – or orbital selectivity - in the cuprates (and other High T_c superconductors, e.g. FeSe) may be pivotal to understanding the microscopic origins and interplay of electronic structure and High Tc. It may also be a natural explanation as to the rarity of High T_c.

The rarity of High Tc: Is a characteristic orbital-selective structure responsible?

A continuing challenge to any understanding of High Tc materials is that, despite the huge advances made since 1987, almost as remarkable as HTS itself, is the fact that the layered cuprates remain the only materials at room pressure that have superconducting transition temperatures above the boiling point of liquid nitrogen [3]. Any satisfactory theory of HTS must therefore explain not only it's microscopic physical origin, which has been the major focus of attention hitherto, but also the equally-striking rarity of the phenomenon exhibited by only a limited number of classes of materials that have been discovered [37, 38].

It is in the reasoning for, and possible explanation behind, this chemical uniqueness we believe that one might find the… "new theme"… that Miguel so powerfully advocated [2].

Pyper and Edwards [37, 38] pointed out that the rarity of HTS could be naturally explained if a highly specific and characteristic electronic structure is needed for hole formation and subsequent hole pairing and for a material to exhibit such superconductivity. And more recently, the concept of orbital-selective Cooper pairing has been invoked to rationalise metallicity and superconductivity in FeSe and related materials [39, 40]. There, also, the pairing arises from electrons of one specific orbital characterwhich bind to form the Cooper pairs of the superconductor. For FeSe, for example, it is predominantly the dyz orbitals of Fe atoms that lead to orbital - selective Cooper pairing [39].

In these models, the pairing of holes or electrons is therefore highly dependent upon the specific atomic orbitals that combine to form the Cooper pairs, which ultimately condense at T_c. As representative, we summarise the basic atomic orbital structure giving rise to both hole- and electron- pairing in the cuprates as well as the oxidised bismuthates (Figure 7).

Thus, in the CuO_2 sheets, the $d_{x^2-y^2}$orbital points directly at the four O_{2-}-ions. (Supplementary Information) All the constituent d orbitals are filled with two electrons except for this $d_{x^2-y^2}$orbital which contains one unpaired electron. Both the modelling [27-30] and quantum chemistry [41-45] approaches show that the hole-doping/chemical oxidation of the CuO_2 sheets brought about by replacement of La_{3+} by Sr_{2+} ions to (ultimately) produce the High Tc material proceeds by the removal of an electron from the highest occupied oxygen py orbitals to leave a Cu_{2+}...O- ...Cu_{2+} subunit whose singly occupied electronic orbitals are depicted in Figure 7 (a).

Since the O-py orbital is orthogonal to both the Cu_{2+} $d_{x^2-y^2}$ orbitals, both the (O-..Cu_{2+}) couplings are ferromagnetic. The direct overlap between a 3d orbital on one Cu_{2+} ion with the corresponding 3d orbital on the other Cu_{2+} ion is almost certainly too small to account for the magnitude of the (strong) antiferromagnetic coupling between the two Cu_{2+} ions. Therefore, this coupling almost certainly arises through a superexchange mechanism involving the filled px and px orbitals on the intervening O_{2-} ion (Figure 6).

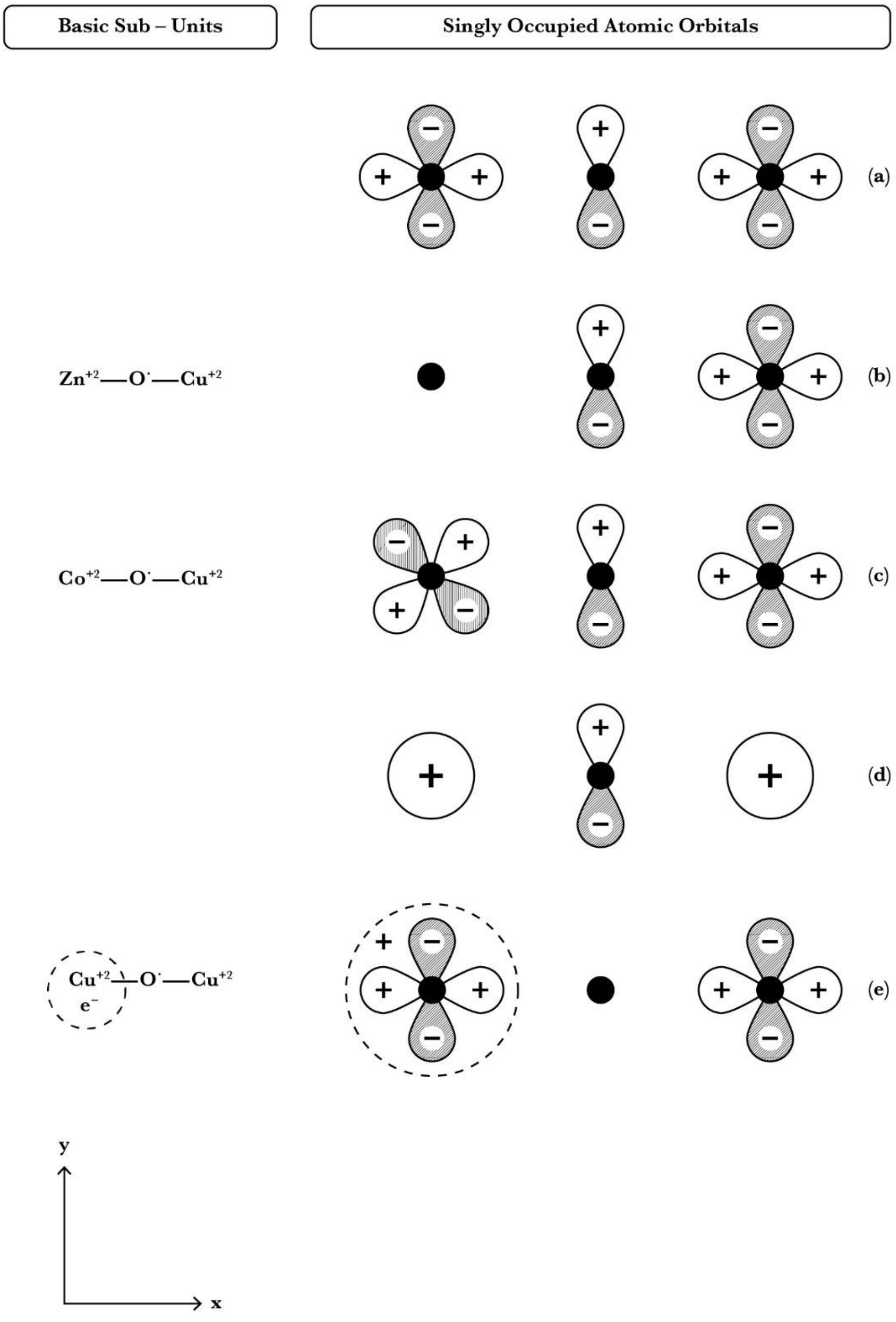


Figure 6. The orbital structures of the fundamental electronic entities considered responsible for high-temperature superconductivity (a) and its suppression by chemical dopants (e.g. (b) Zn^{2+} and (c) Co^{2+}) in the layered cuprates. Also shown is the corresponding situation for the oxidised bismuthates (d) and the electron-doped cuprates (e) from Ref [37].

The necessity for specific, orbital-selective electronic entities (or quasiparticles) considered responsible for HTS in the hole-doped cuprates- also explains its suppression through substitution by chemical dopants (eg Zn^{2+} and Co^{2+}) as well as superconductivity in the oxidised bismuthates and the n-type electron-doped reduced cuprates [37, 38].

This orbital – selective picture naturally links into the proxy bipolaron picture outlined by Catlow et al. [27-30] and provides a natural – and highly specific – mechanism by which these current carrying holes are coupled into the Bose pairs that ultimately condense to yield superconductivity [18, 19].

It is important to note that the oxidation of the O_2-ion in the antiferromagnetically coupled CuO_2 sheets gives rise to characteristic electronic structures that is fundamentally, qualitatively different from those that would be produced if the oxidation were to proceed by ionisation of one of the two Cu_{2+} ions to yield Cu^{3+}. This, in the former case, one would generate a subunit containing three singly occupied orbitals, whereas in the latter, the resulting subunit contains just one unpaired electron [37].

Of most significance here is the proposal that in both the copper-based and iron-based superconducting materials both hole- and electron - pair formation arises from orbital - selective correlations in the normal state from which HTS emerges.

The view we advance, therefore, is that HTS can arise only in materials containing sub-units having such a highly specific orbital structure at a microscopic level. This provides a natural explanation for the rarity of the HTS phenomena and may assist in developing "rules" for looking for other HTS materials (see following section).

A related line of reasoning has been advanced in by Sprau *et al.,* who invoked orbital-selective Cooper pairing of electrons in FeSe, meaning that electrons of only one specific orbital character, there, the dyz orbital of Fe atoms, bind to form the Cooper pairs of the superconductor [39, 40].

There is support that not only the cuprates but also in the strikingly similar family of unconventional superconductors T_c can be shown to scale with the strength of the interaction, J, between nearest - neighbour local moments in their parent antiferromagnetic states. One model has Tc as a product of the strength of this antiferromagnetic coupling as well as the strength of the ferromagnetic coupling [37, 38, 41-45]. Further work is needed in that particular area, building upon the idea of estimating the value of T_c.

A suggested strategy: "A new way of thinking [2]"?

The view we advance is that HTS can only arise in materials containing sub-units of the type noted earlier, having a very special and characteristic electronic structure. On that basis, and thinking primarily of the chemical elements in the d-block of the Periodic Table, our strategy for searching for new families of superconductors can therefore be outlined:

- Search for 2D or nearly - 2D AFM materials that contain local moments whose cation - cation AFM interactions arise from strong superexchange mediated by an intervening anion. Ideally, these next-nearest neighbour AFM magnetic interactions, *occurring between effective spin ½ constituents*, are at least comparable to, but preferably larger than, that found in the cuprates. As noted by DiSalvo [45] this represents a large cation-anion mixing of the wavefunction at the Fermi level. We highlight a major- and critical - focus is that the metal cations comprising the critical sub-units each have an effective spin S = ½.
- Identify classes of these 2D or nearly 2D strongly-antiferromagnetic materials which, upon hole doping will contain those characteristic / fingerprint orbitally-selective units. Such materials will need to be "tuned" by substitutional doping (cation or anion substitution) to

induce p-type hole conductivity to effect a transition to a strange- metallic state across the Mott critical density (Figure 5).

- Think of the resulting combinations of metal atomic orbitals, in association with an 'oxidised anion' – i.e. placing a hole on the anion- (oxide, nitride, carbide- possibly halide) - that can give rise to the basic sub-units having the hole on the anion residing in an orthogonal p orbital next to the metal S=1/2 orbitals (Figure 6 (a) is for the case of Cu^{2+} and an intervening O.-) This characteristic and highly specific orbital-selective electronic structure is then the necessary precursor for both hole formation and subsequent hole-pairing.
- Realise that the generation of the cation S=1/2 state in the AFM material will depend completely upon the normal chemical oxidation state of the metal and upon its local coordination environment. For d-block cations, their crystal field splitting characteristics, with highly distorted near -neighbour environments, must favour non-degenerate states and the required spin-1/2 configuration. Alternatively, the cation valence necessary to produce the necessary spin-1/2 ion can be adjusted through low- to high- crystal field strengths of the surrounding anions or by moving from 1st- to – 2nd-to 3rd row elements. Changing the crystal field strength of the coordinated anion can be tailored to induce the necessary changes in crystal field splitting and the associate high-or low-spin configuration to produce the effective S= ½ state required on the metal cation.

Epilogue

Here, we have highlighted the concept of orbital-selective hole and hole-pair (Cooper pair) formation in the quasi -2D High T_c cuprates and the iron-based superconductors.

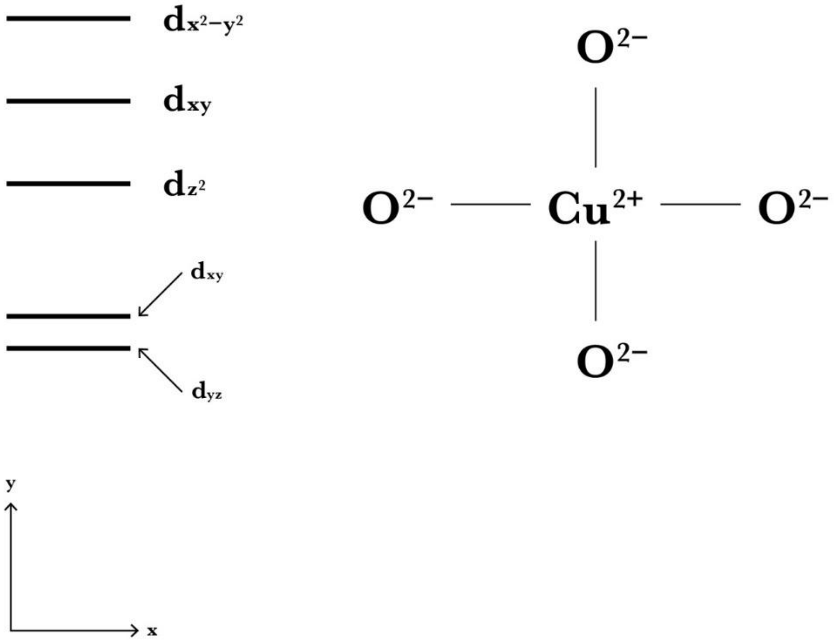
Association of these spinless pairs ultimately yields, through Bose-Einstein Condensation, to a High T_c superconductor. Importantly, such pairs (bosons) exist above the superconducting critical temperature. This orbital - selective Cooper pair formation – and ultimately superconductivity - can only derive from highly specific and characteristic arrangements of orbitals. This orbital – selective interaction visi may be pivotal to understanding the microscopic electronic structure of the pairing mechanism in superconducting cuprate and other materials (e.g. FeSe). It would also account for why- so far- there are only a small number of basic types of superconductors currently known above the temperature of liquid nitrogen.

To remind ourselves of Miguel's 1995 commentary …" experimentalists continue their search (*for other superconductors*) in spite of the lack of a theory and, in this search, imagination, luck, and a combination of both with basic knowledge – something which is often called "chemical intuition "– are usually the commonest tools".

Building on this extant arsenal already in the hands of experimentalists, we hope that our vision of Miguel's " … new theme…" - orbital- selective Cooper pairing to yield bipolarons and their Bose- Einstein Condensation, - may provide the focussed strategy for discovering new classes of materials in which superconductivity emerges at temperatures greater than the highest transition temperature achieved in the cuprate or iron- based superconductors. This is surely one of the major scientific challenges of this century.

Supplementary Material

The crystal-field splitting of the five 3d orbitals characteristic of the high temperature superconducting cuprates



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