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Are Superconductivity Mechanisms a Matter for Chemists?

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Abstract: From a tight-binding approach to the instability of nonbonding electron states, along a double-well potential, we consider here how the coupling of these states with a phonon mode can open a superconducting gap at the Fermi level. The alternation of broken- and unbroken-symmetry states, along the phonon breathing distortion, induces the mixing of band-edge states on a very short timescale, according to the noncrossing rule of chemists. We show that this mixing may generate cationic and anionic disproportionation. The negative $U$ mechanism is thus justified here, leading to the mixing of occupied and unoccupied pair states, for the opening of a $2\Delta$ superconducting gap. The closeness of broad $\sigma^*$ and narrow $\pi^*$ bands in the vicinity of the Fermi level should favor the superconducting phase over the insulating or metallic state, in agreement with Micnas et al.’s studies. We applied this approach to several families of superconducting materials, i.e., doped strontium titanate, high-$T_c$ cuprates and iron selenide.

Keywords: nonbonding electrons; noncrossing rule; negative-$U$ mechanism; phonons; BCS theory; disproportionation; hole pairing; cuprates; titanates; iron selenide

1. Introduction

Are superconductivity mechanisms a matter for chemists? Such a question was a hot topic half a century ago, when the excitonic origin of superconductivity was widely discussed by scientists such as Schafroth, Blatt and Butler [1] or Little [2], in terms of strong interactions in real space (r-space, familiar to chemists). However, the success of the Bardeen–Cooper–Schrieffer (BCS) theory [3], based on a delayed coupling between electrons of opposite spin and momentum, by exchange of phonons in reciprocal space (k-space), was immediately validated by experiment and discouraged many chemists from pursuing the r-space approach. Actually, the BCS theory predicted an upper value of ca. 30 K for the superconducting transition temperature $T_c$. At its early stage, solid state chemistry rather focused on metal-insulator transitions, more spectacular as for example in vanadium oxides in which electric conductivity varies by more than ten orders of magnitude across the transition [4], and is correlated with small crystallographic changes (r-space). This is why many new families of solids, discovered by chemists, were only later found superconducting by physicists. In particular, this was the case of the so-called Chevrel phases discovered by Prigent, Sergent and Chevrel [5], for which superconductivity ($T_c = 15$ K) was evidenced two years later by Matthias [6].

A fourteen-year gap occurred between the synthesis of the first cuprates +III of lamellar perovskite type (Hagenmuller, Goodenough, Pouchard and Demazeau [7]) and the discovery of their superconductivity ($T_c = 32$ K) by Bednorz and Müller [8]; meanwhile, Raveau, Studer and Nguyen [9] had evidenced the key mixed valency +III/+II of copper in these systems. From then on, chemists
participated actively in the so-called “golden rush” for new superconducting families and higher $T_c$ values.

Thirty years later, there is still no consensus on the origin of this unconventional, high-$T_c$ superconductivity: (bi-)polaronic, electronic, magnetic, excitonic, etc. Solving this mystery has been mostly the playground of physicists. However, a few chemists’ concepts were proposed as early as 1987: copper +II disproportionation (similar to silver +II and gold +II) and oxygen to copper charge transfer [10–12], which have remained disregarded.

In 1990, Micnas, Ranninger and Robaczkiewicz [13] published a paper titled “superconductivity in narrow band systems with local non-retarded attractive interactions”, which grabbed the attention of Simon concerning the properties of his rare-earth halogeno-carbides [14]. Actually, Micnas et al. provided an intermediate model, mixture of local pairs and itinerant electrons interacting via a charge-exchange mechanism, giving rise to a mutually induced superconductivity in these systems. Among popular topics in today’s physics are the relations between three types of order, namely magnetism (spins), ferroelectricity (charges) and superconductivity (Cooper pairs); an example is multi-ferroicity. Solid state chemistry and its conceptual framework (structure-bonding-properties) are intrinsically involved in these three types of ordering.

In this article, we present a chemist’s approach to the effect of doping in SrTiO$_3$, which progressively turns from a quantum ferroelectric insulator to a metal and to a superconductor, as recently presented by Rischau et al. [15] and by Gabay and Triscone [16]. Then, while developing further some of our previous work [17], we describe the features underlying the transition from an antiferromagnetic Mott-type insulator such as La$_2$CuO$_4$ into a high-$T_c$ superconductor. Finally, we tentatively apply these approaches to another family of high-$T_c$ superconductors, the iron pnictides/chalcogenides [18,19].

2. A Chemist’s Scenario

2.1. Nonbonding Electrons, from Single to Double Well

Cohesive energies in an ionic-valent solid can be described by a unique potential well, of Lennard-Jones form, with three terms arising from long-range Coulomb forces, short-range van der Waals (attractive) and Born forces (repulsive). As a function of the interatomic distance $d$, these three terms vary as $d^{-6}$, $d^{-12}$ and $d^{-12}$, respectively. A covalent bond, for which the potential well has a single minimum as a function of $d$, can be viewed as a charge accumulation in the interatomic region.

An atomic orbital (AO) basis set is often used to express the electronic structure, i.e., to expand molecular or crystal orbitals. From a molecular or local viewpoint, nonbonding electrons (NBEs) refer to molecular orbitals built on AOs with a vanishing overall overlap $S$. Overlap can be very small alike in $\delta$-type bonding (for example, $xy$-$xy$ along the $z$ direction) or vanish globally by symmetry, as shown hereafter in CO$_2$.

2.1.1. Point Symmetry and the CO$_2$ Molecule

For a CO$_2$ molecule oriented along $z$, let us examine $\pi$-type molecular orbitals built on 2p$\pi$ AOs of carbon and oxygen atoms (labeled O1 and O2). A bonding, a nonbonding and an antibonding molecular orbital, respectively, noted as $1\pi_u$, $\pi_e$ and $2\pi_u$, arise from the three 2p$\pi$ AOs (Figure 1a). The nonbonding character of $\pi_e$ results from the exact compensation of 2p$\pi$–2p$\pi$ overlap integrals $S$, namely, $S(C-O1) = -S(C-O2)$ when the gerade combination of O1 and O2 2p$\pi$ orbitals is considered. If the symmetry is lowered by a displacement of the carbon atom with respect to the center of symmetry, as in a vibration mode, this molecular orbital will no longer be nonbonding, since the overlap integrals no longer compensate. The amplitude of the vibration mode depends on the shape of the potential well for the covalent bond, but also on the atom polarizability (related to Pearson’s hardness in soft/hard chemistry concepts).
2.1.2. Translation Symmetry and Reciprocal Space

The nonbonding character of a crystal orbital can arise from translational symmetry, for a given point or direction in the Brillouin zone. For a regular (TiO)\(\infty\) chain in BaTiO\(3\) along the \(c\) direction of the lattice, according to a tight-binding approach, some crystal orbitals are built on combinations of O 2\(p_x\) and Ti \(d_{xz}\) AOs. Among its quantum numbers, each crystal orbital \(\varphi_k\) is characterized by a wave vector \(k\) that belongs to the first Brillouin zone. If we restrict our example to a one-dimensional chain, then \(k\) is a wave number with \(-\pi/c < k < \pi/c\) and

\[
\varphi_k (r) = \sum_n e^{i k n c} \{ c_1(k). d_{xz}(r) + c_2(k). 2p_x(r) \}
\]

where the integer \(n\) indexes the unit cells, \(c\) is the lattice parameter, \(c_1\) and \(c_2\) are normalization coefficients that depend on \(k\). Figure 1b shows a schematic energy diagram (or dispersion curves) \(E(\varphi_k)\) vs. \(k\) for the two levels or bands arising from the two AOs 2\(p_x\)(O) and \(d_{xz}\)(Ti). At the zone center \(\Gamma\) (\(k = 0\)), 2\(p_x\) and \(d_{xz}\) are not symmetry compatible and the crystal orbitals \(\varphi_k\) are respectively of pure 2\(p_x\) (top of valence band) and pure \(d_{xz}\) (bottom of conduction band) character. The most bonding and antibonding combinations are found at the zone boundaries (\(|k| = \pi/c\)). Therefore, the nonbonding states are found at the zone center, with energies of single O 2\(p_x\) and Ti \(d_{xz}\) AOs, respectively.

Any phonon mode displacing the oxygen atom along \(c\), i.e., shortening vs. lengthening Ti–O bonds, allows bonding and antibonding Ti–O interactions to build up at the top of the valence band and at the bottom of the conduction band, respectively, at \(\Gamma\). Consequently, the band gap increases and nonbonding states no longer exist at the band edges. In this case, the Lennard-Jones potential \(E(q)\) centered at the equilibrium distance \((q = 0)\) superimposes with an off-centered potential \(E'(q)\). The \(q = 0\) position is metastable for \(E(q) + E'(q)\), which has a double-well shape. The double-well depth depends on the magnitude of short-range Born forces, oxygen ion polarizability and overlap/transfer integrals.
Figure 1. Nonbonding states. (a) By point-symmetry compensation: nonbonding π_sym orbitals of CO₂. (b) By translational symmetry compensation: nonbonding crystal orbitals of a (TiO)₅ chain. (c) Nonbonding spin-orbital σₕ for a fragment Cu₂O in a (CuO)₅ chain. Here NBE stands for nonbonding-electron states, while B and AB stand for bonding and antibonding, respectively.

According to the double-well depth, several behaviors arise: (i) the freezing of the phonon mode, into a ferroelectric-type distortion, (ii) an oscillation of the oxygen position, of the “transient crystal structure”-type, or (iii) the tunneling between the two potential wells of small depths. These behaviors were discussed recently by Gabay and Triscone as already cited [16], following a former description of the ferroelectric instability on the basis of chemical bonding, found in the textbook “Chemical Bonding in Solids” by Burdett and in a previous paper by Hoffmann et al. [20].
2.1.3. Multielectron Systems: Hartree–Fock–Roothan Spinorbitals

For a [CuO]⁺ entity in a (CuO)- chain, two combinations of copper \(x^2-y^2\) orbitals are possible, i.e., \((x^2-y^2)_1 \pm (x^2-y^2)_2\), where indices 1 and 2 refer to the two copper atoms. The sum and difference of \(x^2-y^2\) orbitals have gerade (g) and ungerade (u) symmetry, respectively. Only the u combination allows a mixing with oxygen 2p\(\sigma\) orbital, giving a bonding \((1\sigma_u)\) and an antibonding \((2\sigma_u^*)\) molecular orbital (Figure 1c). Here, the oxygen 2s semi-core orbitals were not considered (for further discussion, see Section 4.3.3). Then, the g combination of \(x^2-y^2\) orbitals results in a nonbonding molecular orbital (with respect to Cu-O bonding); it is weakly Cu-Cu bonding. This molecular orbital (noted \(\sigma_g\) hereafter) is expressed in the Hartree–Fock–Roothan formalism, using \(x^2-y^2\) orbitals as basis sets. According to Deutscher and De Gennes [21],

\[
\sigma_g \propto |(x^2 - y^2)_1 \; (x^2 - y^2)_2| + |(x^2 - y^2)_2 \; (x^2 - y^2)_1| + |(x^2 - y^2)_1 \; (x^2 - y^2)_1| + |(x^2 - y^2)_2 \; (x^2 - y^2)_2| \tag{2}
\]

The first two terms are of covalent character and related to the antiferromagnetic coupling between copper sites (Goodenough–Kanamori type). The last two terms are of ionic character and correspond to a \(2\text{Cu}^{2+} \rightarrow \text{Cu}^+ + \text{Cu}^{3+}\) disproportionation, which was proposed in 1987 as a possible origin of Cooper pairs in cuprates (as mentioned in the introduction) [10–12], and which is closely related to the Hubbard parameter \(U\) for electron–electron repulsion. Those ionic terms indicate that, similarly to BaTiO\(_3\), a succession of disproportionate states may occur, making the mid position of the Cu-O-Cu bridge metastable for oxygen; due to the difference in the ionic radii of Cu\(^{2+}\) and Cu\(^{3+}\), the oxygen atom should move away from the doubly occupied single-site orbital (Cu\(^2+\)). As in Co\(_2\), this symmetry breaking allows the oxygen 2p\(\sigma\) orbital to mix with the \(x^2-y^2\) orbitals in \(\sigma_g\), mostly on the Cu\(^{3+}\) site. Phonons will further amplify this symmetry-broken situation, to possibly achieve a permanent distortion at low temperature. Furthermore, cuprates can host other instabilities in which phonons are key parameters, such as Fermi surface nesting and orbital ordering.

From this chemical approach, we conclude that nonbonding electron (NBE) states are very unstable with respect to symmetry-breaking perturbations such as phonons. The electronic structure instantaneously adapts to the atomic oscillations to minimize the energy of the system; as quoted by Maupertuis three centuries ago: “Nature always uses the simplest means to accomplish its effects”. The key question here is the time scale: atomic oscillations occur at the picosecond scale, while electrons visit interatomic distances at the tens of attosecond scale only. Down to which time scale can we talk about succession of states, instead of state mixing?

2.2. Sketching a Chemical Scenario

We emphasized the instability of an NBE state toward static or dynamical distortions in high-symmetry sites. A phonon mode can induce a succession of symmetry-broken and symmetry-unbroken states, with inverse local distortions at each half-period. Obviously, symmetry-broken states last much longer than intermediate high-symmetry states, along one period of vibration. Even if formally instantaneous, we will consider a very short time span \(\delta t\) for the symmetry-unbroken state, with respect to the period.

The period increases along with the softening of the phonon mode; for narrow bands (in underdoped samples), the phonon softening with decreasing temperature leads eventually to an ordered phase, of short or long range, with the freezing of charge transfer, magnetic or orbital order, and stripe or checkerboard-type structures. For broad bands (in over-doped samples), and beside the very short \(\delta t\) time span, the softening should lead to a metallic phase of the Fermi-liquid type. For intermediate band widths, the symmetry breaking induces a gap between the occupied electron band and the unoccupied band. A half-period later, the role of the two bands reverses along with a band crossing. The noncrossing rule (NCR), shown in Figure 2 for discrete states and for crystal orbital states [22], can be retrieved if a superconducting (BCS type) gap opens, which involves the mixing of occupied \((\varphi_o)\) and unoccupied \((\varphi_u)\) pair states, of wave vectors \((k, -k)\) and \((k', -k')\) respectively, according to Whangbo [23]:
\[
< \Phi_u(\mathbf{k}).\Phi_u(-\mathbf{k})|H'|\Phi_u(\mathbf{k'}).\Phi_u(-\mathbf{k'}) >
\]

The nucleation of the superconducting phase will be favored if pseudo-local pair states are also present at the Fermi level, i.e., if the bands above cross a non-dispersive band such as those arising from carbon atomic clusters in rare earth halogeno-carbides (for example in Yt:Ce with \( T_c = 10 \) K [14]).

Figure 2. Schematic representations of the NCR for state \( ^4T_{1g} \left( ^4F, ^4P \right) \) of Cr\(^{3+} \) [22], and for a 1D band with s–p hybridization.

3. Metallic and Superconducting Behavior of SrTiO\(_3\)

From the crystallographic point of view, SrTiO\(_3\) is a perfect perovskite; its Goldschmidt factor is strictly equal to unity. When stoichiometric, SrTiO\(_3\) is a dielectric insulator with the relative permittivity rising to about 20,000 at low temperature, typical of a quantum ferroelectric. The substitution of Ca\(^{2+}\) for Sr\(^{2+}\) (a few \%), with different ionic radii, induces a ferroelectric instability. On the other hand, a slight non-stoichiometry due to oxygen vacancies generates n-type charge carriers and a metallic state, and even a superconducting state below 1 K, despite a very small carrier density [15,24]. Soft phonon modes and oxygen non-linear polarizability were proven to play a key role in the ferroelectric and superconducting properties of SrTiO\(_3\), among other systems [25–27]. As mentioned earlier, there might exist a link between the charge ordering in an insulating ferroelectric phase and the spin/momentum ordering in a superconducting phase. Actually, materials both metallic and polar are scarce and poorly understood so far [16]. In 2017, Rischau et al. proposed that these two kinds of order can coexist upon homogeneous doping, even reinforce each other [15]; however, many works have evidenced inhomogeneous doping in SrTiO\(_3\) as well, resulting in metallic regions coexisting with insulating ones [28–30].

Is there a chemical explanation to those unconventional results? In the first part, we showed how the nonbonding electrons of pure oxygen character, at the top of the valence band, could become partly bonding following a tetragonal distortion of ferroelectric type in BaTiO\(_3\). Conversely, the nonbonding states of pure Ti-character are destabilized; the band gap increases, but the stability of the compound is not affected since the conduction band is empty. The latter argument is no longer valid if electrons are introduced by doping: their destabilization competes with the stabilization of the top of the valence band, and thus with the ferroelectric instability itself. This is observed in tungsten bronzes such as Na\(_x\)WO\(_3\) (0 < x < 1), known for more than a century, in which the ferroelectric
instability of WO₃ disappears progressively for x up to ca. 0.2 [31]. It is therefore understandable that superconductivity in SrTiO₃ remains limited by the extent of electron doping (<0.001). Two preliminary remarks must be made:

(i) The Mott-type insulator-metal transition limits the value of $a_H = \sqrt{n/3}$ close to 0.2, where $n$ is the carrier density and $a_H$ is the Bohr radius corrected by the dielectric constant, as illustrated by Edwards and Sienko [32]. When the dielectric constant is very high, $a_H$ may reach values as high as a micrometer; this is precisely what occurs in SrTiO₃ at low temperature.

(ii) The ferroelectric distortion induces a splitting of the conduction band, namely, $\pi^*(e_g)$ and $\pi^*(b_{2g})$, where $e_g = (xz, yz)$ and $b_{2g} = xy$ (Figure 3).

![Crystal field splitting](image)

**Figure 3.** Crystal field splitting of $t_{2g}$ atomic orbitals from $O_h$ to $C_{4v}$ symmetry, from the ligand field contributions of two axial ligands, unsymmetrically coordinated to the metal ion.

A simple crystal field consideration accounts qualitatively for this band splitting, by summing the potentials in units of $Dq$, the phenomenological parameter used by chemists. The short (axial), the long (axial), and the normal (equatorial) Ti–O interactions are described by the potentials $Dq/(1-k)$, $Dq/(1+k)$ and $Dq$, respectively $(0 < k < 1)$. The band splitting leads to a stabilization of the $b_{2g}$ state ($-6.28k^2$) with respect to the $e_g$ state ($+1.14k^2$). From the point of view of chemical bonding, the Ti$^{4+}$ displacement above (or below) the O plane (i) lifts the degeneracy of $t_{2g}$ states and (ii) decreases significantly the $3d_{xy}/2p$ overlap, decreasing consequently the width of the $b_{2g}$ band (as well known for the VO$^{2+}$ vanadyl ion).

The first carriers then occupy the narrow 2D $\pi^*(b_{2g})$ band, of the fermion character, but also as electron pairs of the boson type, since their Coulomb repulsion on the same orbital almost vanishes ($U = 0$). Their coherence length should be close to the one in BCS-type superconductors such as Nb:Sn (few hundreds nm). Under the phonon modes discussed above, those pseudo-local pairs, which are not yet proper Cooper pairs, mix, at each ¼ period, with empty $t_{2g}$ states arising from $t_{2g} = b_{2g} + e_g$. Then, they can separate according to $b_{2g}^2 \rightarrow b_{2g}^1 + e_g^1$ (“$t_{2g}^{\delta\pi}$”) into a Fermi liquid, or mix with empty $e_g$ or $t_{2g}$ states according to $b_{2g}^2$ (pseudo-local pairs) + $t_{2g}^0$ (“$t_{2g}^{\delta\pi}$”) into Cooper pairs with opening of a superconducting gap.

$$< b_{2g}^1(k) \cdot \bar{b}_{2g}^1(-k) |H'| t_{2g}^0(k') \cdot \bar{t}_{2g}^0(-k') >$$

(4)

In essence, the ferroelectric instability (provided by the small doping of Ca$^{2+}$ and by the nonbonding character of electrons at the top of the valence band) induces a bistable electron system coupled to the oscillations of the axial oxygen atom. Here, we had all the ingredients for a two-band scenario, with a broad and a narrow band; the first band consists of empty states, the second contains
electron pairs due to $U \approx 0$ and a large dielectric constant. The two bands mix before the gap closure, into a superconducting state even with such low carrier densities as $10^{17}$ cm$^{-3}$.

A simple electronic Hamiltonian $H^\prime$ replaces here the (delayed) electron–phonon coupling Hamiltonian of the BCS model. This chemist’s view applies to SrTiO$_3$-LaAlO$_3$ heterostructures as well, justifying the intrinsic doping and the ferroelectric-type distortions expected in these structures. SrTiO$_3$ can be viewed as a succession of neutral TiO$_2$ and SrO layers; LaAlO$_3$, a perovskite as well, has charged AlO$^-$ and LaO$^+$ layers. Thus, the interface of the heterostructures can be regarded as a charged layer La$_{0.5}$Sr$_{0.5}$O$^{0.5}$. The electric field gradient between LaO$^+$ and neutral SrO layers should be screened, as in $p-n$ junctions, by a charge transfer: TiO$_2$ + AlO$^-$ $\rightarrow$ (TiO$_2$)$^+$ + (AlO$_2$)$^{2-}$, which is actually a charge transfer between O$^-$ (AlO$_2$) and Ti$^+$ (TiO$_2$); the $e^+/h^+$ pair opposes then the electric field gradient.

Additionally, the Ti-O-Al entity is disymmetric in terms of chemical bonding and, in the same way as a ferroelectric distortion, induces both a band splitting from $t_{2g}$ to $b_{2g}$ and $e_g$ and a dynamical polarization of TiO$_2$ layers away from the interface. Therefore, the first nonbonding electrons in the conduction band ($t_{2g}$) will undergo a succession of quasi-local pair states ($b_{2g}$, few hundreds nm) and delocalized Cooper-pair states, due to the mixing with empty $e_g$ or $t_{2g}$ states when the gap closes. Such a description is close to that of Gariglio et al. [33] in their review on interface superconductivity.

### 4. High-¥Tc Superconducting Cuprates

A significant difference between cuprates and titanates is the one-electron energy (Coulomb integral) for 3d orbitals. The Ti and Cu 3d states lie respectively above and below the O 2p state, which affects the electronic structure: in cuprates with optimum doping, the valence band should be of dominant Cu-character, the conduction band being mostly of oxygen character.

La$_2$CuO$_4$, the structural parent of superconducting cuprates, is a charge transfer insulator with a first excited state described by $O^2- + Cu^{2+} \rightarrow O^+ + Cu^+$. It is also an antiferromagnet with a Néel temperature close to the ambient temperature. La$_2$CuO$_4$ is mostly p-doped by substitution of Ba$^{2+}$ or Sr$^{2+}$ for La$^{3+}$, or by chemical or electrochemical intercalation of oxygen in La$_2$O$_3$ rock salt-type layers. Doping of 8–20% induces a metallic then superconducting state ($T_c \approx 40$ K), along with a significant decrease in the unit cell volume; shortened interatomic distances lead to larger $t_{2g}$-o transfer integrals and thus to larger band widths, but also to stronger oxygen–oxygen interactions that turn out to be of major relevance here. Along with doping, the band widths increase and the value of the Hubbard parameter decreases due to covalency ($U$ is related to Racah repulsion parameters $B$ and $C$, familiar to chemists, and sensitive to covalency); this is consistent with an insulator-metal transition of the Mott–Hubbard type, for increasing the $U/T$ ratio.

We start from this framework, with $U \approx 0$, to describe the electronic structure of cuprates with optimum doping (i.e., formally Cu$^{2+}$-$\gamma$ with $\gamma$ close to 0.15). $U \approx 0$ means a full $O^2- + Cu^{2+} \rightarrow O^+ + Cu^+$ transfer, Cu$^+/O^-$ being the ground state. This is justified by several arguments:

(i) Coulomb integrals, $H_{4d}(Cu) = -18.7$ eV and $H_{4p}(O) = -17.1$ eV [34]. Tight-binding calculations for (CuO)$_6$ square planar clusters, as found in La$_{1-x}$Li$_x$CuO$_2$ [35], show clearly this charge transfer situation (Figure 4 in Ref. [36]).

(ii) Doped holes in cuprates are essentially located on oxygen atoms, as demonstrated by the pioneering work of Bianconi et al. [37] by X-ray absorption spectroscopy (XANES), later on by electron-loss spectroscopy (EELS) [38] and by spectacular atomic scale imaging from tunneling asymmetry, even on underdoped samples, by Hanaguri et al. [39], Kohsaka et al. [40] and Pasupathy et al. [41], showing inhomogeneous charge distributions as nano-scale stripes or checkerboard patterns on oxygen atoms.

(iii) Recent studies by Jurkat et al. [42] using NMR on $^{63-65}Cu$ and $^{17}O$ doped samples, leading to a phase diagram for $T_c$ as a function of the distribution of doped holes at Cu and O sites.
4.1. (CuO$_{2}$)$_{2}^-$ Unit Cell

The input data for our tight-binding calculations are reported in Table 1. Figure 4 (top) shows the dispersion curves $E(k)$ in the $-19$ to $-15$ eV range. Several bands are identified:

(i) Around $-19$ eV, a valence band of Cu character and Cu-O bonding interactions.
(ii) Between $-18$ and $-15$ eV, a broad conduction band of oxygen character, and Cu-O generally antibonding.

\[ \text{Figure 4. Top: Dispersion curves } E(k) \text{ for a (CuO$_{2}$)$_{2}^-$ unit cell, from tight-binding calculations. Bottom: Brillouin zones for the single and double unit cells (BZ1 and BZ2), and their high symmetry points.} \]
Table 1. Parameters for extended Hückel tight-binding calculations: $H_i$'s are the diagonal matrix elements of the effective Hamiltonian, $\zeta_i$'s and $c_i$'s are respectively the exponents and contraction coefficients for the Slater-type atomic orbitals (AOs).

| Element | AO  | $H_i$(eV) | $\zeta_1$ | $c_1$ | $\zeta_2$ | $c_2$ |
|---------|-----|-----------|-----------|------|-----------|------|
| Cu      | 4s  | −7.44     | 2.151     | 0.48071 | 1.168     | 0.61474 |
|         | 4p  | −4.26     | 1.370     | 1.0   |           |       |
|         | 3d  | −18.7     | 7.025     | 0.44221 | 3.004     | 0.68886 |
| O       | 2s  | −33.7     | 2.246     | 1.0   |           |       |
|         | 2p  | −17.1     | 2.227     | 1.0   |           |       |
| Fe      | 4s  | −9.1      | 1.900     | 1.0   |           |       |
|         | 4p  | −5.32     | 1.900     | 1.0   |           |       |
|         | 3d  | −12.6     | 5.350     | 0.55050 | 2.000     | 0.62600 |
| Se      | 4s  | −20.5     | 2.440     | 1.0   |           |       |
|         | 4p  | −13.2     | 2.070     | 1.0   |           |       |

Figure 5 shows an enlarged view of the two top bands, between −17 and −15 eV, noted here $\sigma^*(b_{1g})$ and $\pi^*(a_{2g})$ (as referred to the point symmetry of the copper site, at the M1 point of BZ1). At Γ, these two bands are degenerate and of pure oxygen character (Figure 5a). The top band, $\sigma^*(b_{1g})$, is broad ($W \approx 1.5$ eV) due to strong Cu-O and O-O antibonding interactions; the $\pi^*(a_{2g})$ band is narrow ($W \approx 0.3$ eV) because of its Cu-O nonbonding character (especially in Γ, M1) or by compensation of Cu-O and O-O antibonding/bonding interactions (in X1).

The $E(k)$ vs. $k$ plot for $\sigma^*(b_{1g})$ shows a saddle point in X1, associated with a van Hove-type peak in the density of states (this point will be discussed later). The corresponding crystal orbital has contributions from Cu 4s, $z^2$ and $x^2−y^2$ with respective weights of 0.037, 0.088 and 0.252. The 4s/3z$^2$ hybridization is well known for the Jahn-Teller Cu$^{2+}$ ion. The other contribution is from the 2p$_{x}$ orbital of one oxygen, with a weight of 0.650. Thus, the oxygen character is approximately twice the copper character in this crystal orbital, and the bonding is strongly anisotropic with large antibonding interactions along [100] and nonbonding interactions along [010] (Figure 5e). This nonbonding character in X1 offers the possibility of opening a static or dynamical gap of nematic type (a ≠ b), with the creation of a double-well potential as in SrTiO$_3$. For the Fermi level to be located in X1 for the $\sigma^*(b_{1g})$ band, a hole doping rate of 12−15% should be necessary. This approach, which agrees with experiment, does not discriminate electrons and doped holes; doping is used to shift the Fermi level toward a high-symmetry point of the Brillouin zone.
Figure 5. (a) Enlarged view of the two upper \( \sigma^*(b_{1g}) \) and \( \pi^*(a_{2g}) \) bands of Figure 4 with (blue) and without (red) participation of oxygen 2s AOs. Representations of the crystal orbitals belonging to single and double unit cells (indexed 1 and 2, respectively): (b) \( \sigma^*(b_{1g}) \) crystal orbital in M1(\( \Gamma_2 \)) with \( b_{1g} \) and \( a_{2g} \) symmetries for the copper occupied and non-occupied sites, respectively. (c) \( \pi^*(a_{2g}) \) crystal orbital in M1, with \( a_{2g} \) and \( b_{1g} \) symmetries for the copper occupied and non-occupied sites, respectively. (d) Crystal orbital at the saddle point in M2, with two different copper sites of \( b_{1g} \) (1) and \( a_{1g} \) (2) symmetry; in the middle, oxygen lies in a strongly asymmetric environment—a Janus atom, with a large 2p-(\( x^2−y^2 \)) overlap vs. a small 2p-\( z^2 \) overlap; O–O interactions are antibonding around \( b_{1g} \) and bonding around \( a_{1g} \). (e) Crystal orbital with same anisotropy in X\( _1 \) than (d), but not leading to 1:1 orbital ordering, by differentiating [\( 100 \)] from [\( 010 \)] directions. (f) Eight molecular orbitals for a square \( O_4 \) group, considering 2px and 2py only. (g) Role of oxygen 2s orbitals, decreasing the anisotropy found in (e).

4.2. The Double Unit Cell (Cu:O\( _4 \))

Figure 5a shows the same dispersion curves \( E(k) \) for a double unit cell (Cu:O\( _4 \)) but with a different crystal orbital distribution in the two unit cells. The hybridization of \( z^2 \) and \( x^2−y^2 \) reinforces the anisotropy of the (anti)bonding between copper and oxygen (Figure 5e). Besides, we can consider the hypothesis of a distribution of those two orbitals over two distinct sites (orbital ordering).

The correspondence between the Brillouin zones and high symmetry k-points of the single (BZ1, M1, X1...) and double unit cell (BZ2, \( \Gamma_2 \), M2...) is shown in Figure 4 (bottom).
The M2 point, corresponding to X1 for the single unit cell, shows a degeneracy between an energy band arising from $\sigma^*(b_{1g})$ (M1 corresponds to $\Gamma_2$) and a lower energy band arising from $2e_u$ ($\Gamma_1$). Both bands show a full and opposite orbital ordering on copper sites labelled (1) and (2) (Figure 5d), and appeared isotropic since the weights on oxygen atoms were identical. The symmetries on the two copper sites were different: $a_{1g}$ and $b_{1g}$, which confirms the proposed 1:1 orbital ordering. Each oxygen atom, overall nonbonding, becomes a Janus entity, bonding on one side (with respect to $a_{1g}$ O-O bonding) and Cu-O antibonding on both sides, but weakly in $a_{1g}$ ($c_i^2 = 0.15$), stronger in $b_{1g}$ ($c_i^2 = 0.22$), thus fully disymmetric. Compared to X1 (spatially dissymmetric, antibonding/bonding along [100] and nonbonding along [010] (Figure 5e), with the reverse situation at Y1), M2 does not show any tendency to nematicity, but rather a strong tendency to couple to an optical mode of breathing type, with a dynamical inversion of the copper sites (1) and (2) (Peierls-type 2D instability); a tight-binding calculation (EHTB) leads to a gap opening of 33 meV per pm of phonon amplitude.

We too had here a critical hypothesis, with an oscillating band gap driven by a phonon mode. At each half-period, the two bands cross; at this very moment, the noncrossing rule suggests the opening of an electronic gap, followed by a superconducting gap $2\Delta_{SC}$ by mixing the two bands according to:

$$< e_u^1(k) \cdot e_u^1(-k) \cdot H' \cdot b_{1g}^0(k') \cdot b_{1g}^0(-k') > \quad (5)$$

Figure 6a shows the evolution of the ground state along a phonon half-period ($-\pi/2$ to $+\pi/2$), from a $b_{1g}$ ($a_{1g}$) enlarged (compressed) site, as a function of the oxygen displacement $\delta$. Two types of domains can be observed: (i) on both sides, a smooth evolution of the $e_u$ and $b_{1g}$ band edges with $\delta$; (ii) in the middle, a progressive mixing of $e_u$ and $b_{1g}$, up to a full reversal. Figure 6b represents the crystal orbitals before and after mixing for a 50:50 ratio.

The hybridization of $x^2−y^2$ and $z^2$ favors one direction out of [100] and [010], as observed above in X1, and evens the weights on both copper ions; conversely, it strongly discriminates the four oxygen atoms, two of them with vanishing crystal orbital coefficients. However, as we will discuss later, this charge ordering is likely to vanish partially by delocalization of the two holes among an $\text{O}_4^{2-}$ cluster. From the above, it can be stated that such crystal orbital mixing leads to a charge transfer through electron (hole) pairs.

Another important feature is the high polarizability of $\text{O}^{2-}$, whose electronic dipole (due to its Janus character) may oscillate at high frequency, a few orders of magnitude faster than phonons. Such a behavior can be considered as the result of the O(2p)/O(2s) hybridization (Figure 6c). This dipole oscillation may contribute, as in atomic spinodes, to induce a decomposition into various components of the $e_u/b_{1g}$ mixtures in equilibrium, exchanging hole pairs, and consequently leading to the Whangbo Hamiltonian of pair-occupied and pair-unoccupied states [23,43].
Figure 6. (a) Effect of the NCR along the phonon $\phi$ of amplitude $\delta$. On the left side, the occupied $e_u$ band with large $b_{1g}$ and small $a_{1g}$ sites. On the right side, the same sites for the inverse $\delta$ and the occupied $b_1$ band. (b) Mixing the two bands at 50/50 and $\delta = 0$ evens the copper charges and conversely differentiates strongly two among four oxygen atoms, inducing charge fluctuations. Hole doping creates $(O_4)^{5-}$, which should disproportionate into $(O_4)^{6-}$ and $(O_4)^{4-}$. (c) Oxygen dipole reversal induced by the $2s$–$2p$ hybridization and the phonon $\phi$. 
4.3. The $\pi^*(a_{2g})$ Band

As proposed in 1990 by Micnas et al. and later illustrated by Simon [13,14], the crossing of a broad and a narrow band close to the Fermi level would be a key factor for the coupling of quasi-local pairs (narrow band) and fermions (broad band), to form Cooper pairs. Could the narrow, 300 meV-wide $\pi^*(a_{2g})$ band, which lies approximately 400 meV below the Fermi level, be raised to the Fermi level and generate local electron pairs? For this band, Figure 7 illustrates: (i) in X1(M2): the $a_{2g}$-$b_{2g}$ orbital ordering, with overall O–O nonbonding character and Cu–O antibonding character at the $b_{2g}$ site; (ii) in M1: the $a_{2g}$ symmetry of each copper site, for which oxygen atomic orbitals show $b_{1g}$-type overlap on vacant cationic sites (½ ½ 0) with an antibonding O–O character identical to the $\sigma^*(b_{1g})$ band for copper (see also Figure 5c).

![Diagram showing crystal orbitals of the narrow $\pi^*(a_{2g})$ bands at X1 (M2) and M1 points of the BZ.](image)

**Figure 7.** Crystal orbitals of the narrow $\pi^*(a_{2g})$ bands at X1 (M2) and M1 points of the BZ.
4.3.1. Positioning of the $\pi^*(a_{2g})$ Band

The $(\text{CuO})^{2−}$ layer is sandwiched between so-called reservoir layers, in which the doping adjusts the amount of charge carriers in the CuO$_2$ layer. Additionally, being ionic, these reservoir layers generate an electrostatic (Madelung) potential that can be estimated by the Ewald summation method. One has to consider as well the screening of the Madelung potential by the charge carriers of the conducting layer; therefore, we restricted the calculation of Madelung potentials to the contribution of a few neighbor cells, and considered orders of magnitude only.

It is also straightforward to compare the importance of the Cu-O charge transfer in CuO$_2$ layers, by considering three cases of the Madelung terms: Cu$^{2+}$/O$^{2−}$, Cu$^{4+}$/O$^{2−}$ and Cu$^{2+}$/O$^{−}$. A few comments arise from these rough calculations: (i) as expected, the potential at the copper site is negative, whichever the Cu-O charge transfer case is; (ii) the potential at the oxygen site is positive, except for the insignificant Cu$^{2+}$/O$^{−}$ case, and iii) at the vacant cationic site ($\frac{1}{2}$ 0 0), which will be labeled (+) in the following, the Madelung potential, $V_M(+)$, is negative to whichever the charge transfer case is, but is lower by ca. 1/3 than the potential at the occupied site, in absolute value. This justifies a specific treatment for the antibonding electrons in the $\pi^*(a_{2g})$ band; iv) the negative character of $V_M(+)$ increases when the apical Cu-O distance (i.e., the separation between the CuO$_2$ and the reservoir layer) increases. Therefore, the negative Madelung potential reinforces the destabilization of electrons at the vacant cationic site, adding up to the antibonding character of the O–O interactions. These features should favor the stabilization of doped holes near the vacant ($\frac{1}{2}$ 0 0) cationic sites of the CuO$_2$ layer. How many holes? Can we envisage a hole pair on oxygen entities as well known for electrons and in $b_{2g}$ of electron doped SrTiO$_3$, i.e., a dimerization $(\text{O}_2)^{2+} + (\text{O}_2)^{2−} → (\text{O}_2)^{2+} + (\text{O}_2)^{2−}$? We would then obtain what chemists would call a hole lone pair, or an antiatom with a pseudo negative nucleus arising from $V_M(+) ≤ 0$; the two holes would then again have a wave function of $x^2−y^2$ type of $b_{1g}$ symmetry.

These distortions appear perfectly with features revealed by Bianconi et al. [44] from extended X-ray absorption fine structure (EXAFS) spectroscopy on La$_{1.85}$Sr$_{0.15}$CuO$_4$ crystals, showing a heterogeneous stripe system with an accumulation of hole carriers in a region with elongated apical and shortened equatorial Cu-O bonds (2.40 Å and 1.88 Å, respectively).

4.3.2. Mulliken–Jaffé Electronegativity for Oxygen

In M1, the $\pi^*(a_{2g})$ band is of pure oxygen character. We can express the energy $E(q)$ of the oxygen ion as a function of its charge $q$, its electronic affinity $E_A(q)$ and its ionization energy $E_I(q)$:

$$E(q) = \alpha \cdot q + \beta \cdot q^2 + \gamma \cdot q^3$$  \hspace{1cm} (6)

where $\alpha = \frac{1}{2}(E_I(q) − E_A(q))$ is the Mulliken electronegativity, $\beta$ is Pearson’s hardness and $\gamma$ is an adjustable parameter; for oxygen, $\alpha = 6.925$, $\beta = 6.190$ and $\gamma = 0.505$. $E(q)$ is plotted on Figure 8. The Mulliken–Jaffé electronegativity $\chi_M$ is defined as the derivative of $E(q)$ with respect to $q$. As seen in Figure 8, $\chi_M$ vanishes for $q = −0.6$ and is negative below this $q$ value. Additionally, it shows that O$^{2−}$ is not stable in the gaseous phase, and will likely lose an electron at the surface of an oxide—catalysts take advantage of this effect.

Therefore, to account for the electronegativity of oxygen in an ionic-covalent lattice, it is necessary to add a Madelung-type term in Equation (6). The magnitude of this term is difficult to estimate, since outer electrons of oxygen lie away from the exact atom site. Since the Madelung energy is proportional to $q^2$, we will use the corrected expression

$$E(q) = \alpha \cdot q + (\beta − k) \cdot q^2 + \gamma \cdot q^3$$  \hspace{1cm} (7)

for the energy of the oxygen ion as a function of its charge $q$. Figure 8 illustrates the importance of this Madelung term: (i) the minima are displaced toward the most negative charges (most ionic configurations), (ii) $E(q)$ vs. $q$ curves flatten, around their minima, until $k ≈ 3$ and the appearance of an inflexion point. If we start from the $(\text{O}_2)^{2+}$ cluster, oxidized into $(\text{O}_2)^{2−}$ by charge transfer, at the X-point of the BZ, its progressive oxidation by doping into $(\text{O}_2)^{2−}$ then $(\text{O}_2)^{2+}$ corresponds to a maximum 0.5 electron per oxygen, for example between O$^{−}$ and O$^{1.5}$, whose formation energies $E(q = −1.0)$ and
$E(q = -1.5)$ do not differ by more than 50 meV (Figure 8). This energy difference is less than the O–O resonance energy, which can be estimated to be approximately a hundred meV (Figure 4 of Ref. [36]); this leads to $U < 0$, as in the negative-$U$ model for superconductivity [45].

**Figure 8.** Formation energy $E(q)$ of an O$^q$ ion ($-2 < q < 1$), related to the Mulliken–Jaffe electronegativity $\chi_{MQ}$ for the free ion ($k' = 0$) and for the ion embedded in a Madelung potential ($k' \neq 0$).

According to the above discussion, we can describe the electronic structure of (CuO$_2$)$_2^-$ layers by a network of O$_4$ square planar entities (Figure 9), which provide the four sets of molecular orbitals ($b_{1g}$, $a_{2g}$), ($1e_u$, $2e_u$) and ($a_{1g}$, $b_{2g}$) as indicated in Figure 5f (by neglecting the out of plane $2p_z$ orbitals), in order of decreasing energy. In this network, cationic sites are either (i) fully occupied by Cu$^{2+}$ ions, in the tetragonal epitaxial form of t-CuO, (ii) half-occupied by Cu$^{2+}$ in high-$T_c$ cuprate layers, (iii) one-fourth occupied by Cu and one-fourth by Li$^+$, in an ordered manner, in insulating LaLiCuO$_8$, which can be described in terms of (Li$^+$)(Cu$^{2+}$)(O)$_4$$^{-}$ layers ($I4/mmm$), with two holes in the $\sigma^*(b_{1g})$ molecular orbital centered on each Cu$^+$ ion. At low $T$, this phase undergoes an orthorhombic distortion ($Ammm$), from $D_4h$ to $D_2h$ for Cu$^+$ and Li$^+$ ions, with a buckling of distorted sites. Besides, the buckling of square-planar entities splits the unoccupied cationic sites (+) into two types of sites of the same $D_3$ symmetry but a different size (labeled hereafter L and S). This atomic distortion and the increase in antibonding at the S site are reinforced by a 2p–2s oxygen orbital hybridization towards the S site (see below). These two situations can be transposed to the distortions of the O$_4$ network of the (CuO$_2$)$_4^-$ layer, with a breathing mode (arrows in Figure 9) but also a “hole disproportionation” and octahedra buckling ($2a_{2g}^{-} - a_{1g} + a_{2g}$); this $\pi^*(a_{2g})$ band, already narrow (ca. 300 meV) and further split by phonons, should serve as a seed for Cooper pairs delocalized in the broad $\sigma^*(2e_u)$ band of the
superconducting phase. This hole-acceptor character of $\pi^*(a_{2g})$ agreed with the statement of Hirsh et al. for locating the cuprate holes preferentially in the oxygen $2p_\pi^*$ bands [46,47].

![Diagram](image)

Figure 9. $\{([\text{Cu,Li}]\text{O}_5)^{2-}\}$ layers built from $(\text{O}_4)^{2-}$ square planar entities, with ordering or buckling, illustrating charge transfer as well as charge disproportionation possibilities. The small (S) and large (L) O$_4$ squares represent such a case for $(\text{O}_4)^{2-}$ groups.

4.3.3. Role of Oxygen 2s Atomic Orbitals

So far in our discussion, the role of semi-core (or rather deep-valence) 2s orbitals of oxygen was not discussed; by introducing them in the tight-binding calculations, we noticed that the energy at X1 shifted upward by ca. 500 meV (blue line in Figure 5a) due to $z^2$(Cu)-2s(O) antibonding interactions along [010] (Figure 5g). Such a 2s ± 2p hybridization modified the electron density in the vicinity of the oxygen ion, increasing the Cu-O antibonding character of the band in an asymmetric way and contributing significantly to the Janus effect. In an axially distorted ($a_{1g}$) Cu$_2$O$_4$ cell, for example, the 2s ± 2p hybridization reinforced the strong antibonding interactions with $x^2-y^2$, while it weakened the already weaker antibonding interactions with the equatorial lobe of $d_{z^2}$ orbitals. Overall, this favored the charge transfer from oxygen to copper.

Similarly, for the $Ammm$ transverse distortion, the 2s ± 2p hybridization reinforced the strong antibonding O–O interactions in the small (S) square planar O$_4$ groups, while weakening them in the large (L) ones. This favors the introduction of doping holes in this region of cationic type (negative value of the Madelung potential $V_M$), even their pairing. Additionally, a much smaller hole density is necessary to reach the X1 point; it actually corresponds to a slight electron-doping (as in n-type cuprates). The contribution of 2s orbitals will be modulated by the competing oxygen-rare earth
bonding. The important role of oxygen 2s orbitals had already been mentioned many years ago with respect to the gap value for the parent insulating phase [48].

4.4. Underdoped Cuprates

The phase diagram is complex (pseudo-gap, charge density waves, stripes, checkerboard patterns, etc. [49,50]); however, those phases should be related to characteristics of the pristine La$_2$CuO$_4$ phase. La$_2$CuO$_4$ is an insulating antiferromagnet of Mott or rather charge-transfer type, in which the lowest excitation involves the gap between the oxygen-character band and the upper Hubbard band: $O^2^- + Cu^{2+} \rightarrow O^- + Cu^+$. This charge transfer can be symmetric, leading to an antiferromagnetic coupling by superexchange. We will examine the non-symmetric transfer only, which involves two copper ions (labeled 1 and 2) according to:

\[
\begin{align*}
\uparrow Cu(1)^{2+} + O^2- + \downarrow Cu(2)^{2+} & \rightarrow Cu(1)^+ + \uparrow O^- + \downarrow Cu(2)^{2+} \quad \text{(U), or} \\
\uparrow Cu(1)^{2+} + O^2- + \downarrow Cu(2)^{2+} & \rightarrow \uparrow Cu(1)^{2+} + \downarrow O^- + Cu(2)^+ \quad \text{(D)}
\end{align*}
\]

where the arrows indicate the spin orientation. The remaining spin on oxygen couples with the spin $\frac{1}{2}$ on Cu(2), in a bonding state in Equation (8), in the same way as the Zhang and Rice singlet (ZRS) description [51] in the well-known $t$-$J$ model. The charge transfer (CT) of this type will be noted CT-ZRS(U) or CT-ZRS(D), by reference to the remaining spin of the oxygen ion. This transfer breaks the $C_2$ symmetry of the Cu-O-Cu bridge, Cu$^+$ being larger than Cu$^{2+}$ associated to O$^-$. Thus, we can imagine a local two-dimensional 1:1 order of CT-ZRS(D) and CT-ZRS(U), which can be static or coupled to a phonon mode (see Figure 10). Three remarks arise:

(i) The charge transfer rate is formally 50% (i.e., half the optimal doping value),

(ii) One magnetic network over two must disappear at each phonon half-period; this scheme is consistent with the sharp decrease of Néel temperature with doping,

(iii) Local ordering domains appear (U or D), separated by antiphase boundaries, and alternating at each half-period.

Figure 10 (bottom) illustrates these two situations. What is the role of doping? At each half-period, when the symmetry is not broken, doping holes can form as many ZRS-[u] as ZRS-[d] ($y$-axis in Figure 10). However, the formation of CT-ZRS (either D or U) at each quarter-period, on each side of the antiphase boundary, is only compatible with doping holes of the opposite norm (d/U or u/D), thereby rejecting doping holes of the same norm (d/D or u/U) toward the other domain.
Figure 10. Phase diagram for a non-symmetric charge transfer (CT) in under-doped cuprates, as a function of hole doping (represented as usual by a Zhang–Rice singlet (ZRS) [39], and denoted as [u] or [d] according to the remaining oxygen spin) and CT between two copper atoms (denoted U and D as previously). The diagram shows avoided areas, from where some doping holes ([u]/[U] or [d]/[D]) are expelled toward another CT-type part of the crystal, giving rise to hole transfer of opposite spin and momentum (Cooper pairs).

In essence, this is a collective displacement of holes of opposite spins (u vs. d) in opposite directions (+k vs. −k), i.e., characteristic of Cooper pairs for a possible superconducting state. Note that this mechanism leads to a density of pairs, which is half the expected value, as seen experimentally [52].

In conclusion, this model agrees with the description by Reznick [53] titled “Electron-phonon coupling reflecting dynamic charge inhomogeneity in oxide superconductors”, invoking strong bond stretching phonon anomalies common to stripe-ordered and superconducting materials, between ordered magnetic and hole-free layers, and charge transferred Cu⁺ and hole-rich oxygen ones.

5. Iron Arsenides and Selenides

As early as 1965, Bertaut reported the anomalous nonmagnetic behavior of FeS, a rare mineral of mackinawite type, first identified in 1962 [54]. Due to its low thermal stability, FeS is difficult to obtain as a pure phase (i.e., without metallic iron as impurity). Besides, not long after the discovery of high-Tc superconductivity in the doped pnictide LaO1−xFexAs (Tc = 26 K) by Hosono et al. in 2008 [55], the selenide β-FeSe showed superconductivity below c.a. 10 K. FeSe has the same mackinawite (P4/nmm) structure as does FeS, but is more stable. Furthermore, Tc in FeSe can reach 30 K either under pressure or upon S-Se substitution; both conditions correspond to a decrease in the unit cell volume, as often observed for the spin transition S = 2 → S = 0 in ferrous materials [56].

We chose to apply our tight-binding approach to FeSe, to check if similar features arise in the case of chalcogenides, as found in our analysis of the titanates and cuprates. The tight-binding parameters for Fe and Se are listed in Table 1. The values of Coulomb integrals for Fe 3d and Se 4p orbitals lie within 0.6 eV, indicating a strong covalency for Fe–Se bonds. This justifies the use of a
vanishing ($U = 0$) Hubbard parameter for electron–electron repulsion, although a nonzero $U$ value would have to be considered for crystal orbitals of pure Fe character, at certain points of the Brillouin zone.

Figure 11 shows the crystal structure of $\beta$-FeSe. The iron atoms form a square plane network identical to the one found for the oxygen atoms in cuprates, an essential feature for our scenario of high-$T_c$ superconductivity. However, the cationic vs. anionic character of Fe vs. O limits this analogy; in particular, the $E(q)$ curve for iron cannot show a minimum near $q = 2$ (see Figure 8 for oxygen). Additionally, the cationic sites differ from an elongated octahedron ($D_{4h}$) or a pyramid ($C_{4v}$) in cuprates to a slightly elongated tetrahedron ($T_d$) in iron selenides or slightly compressed in iron pnictides. The distortion of the FeSe$_4$ tetrahedron lifts the degeneracy of the iron $t_2$ orbitals into an $e$ doublet (xz, yz) and a $b_2$ singlet (xy), only partly compensated by the crystal field ($D_{4h}$) of the four Fe$^{n+}$ next-neighbors (at the distance of 2.67 Å).

Figure 11. Scheme of the low-temperature structure of $\beta$-FeSe ($P4/nmm$) with edge-sharing FeSe$_4$ tetrahedra in the $ab$ plane (left), and the succession of layers along c (right).

Figure 12 shows the dispersion curves obtained from the tight-binding calculations for a Fe$2$Se$_2$ primitive cell; the Fermi level is situated at $-11.74$ eV. Several band stacks can be identified, in order of increasing energy: (i) around $-21/-22$ eV, two Se 4s-character bands (not represented in the figure); (ii) between ca. $-15.5$ and $-14$ eV, six rather narrow Se 4p-character valence bands, with a significant Fe contribution and iii) broad conduction bands, divided in two stacks (according to the bonding or antibonding Fe–Fe interactions) that overlap slightly at $\Gamma 2$ and $M 2$ points, close to the Fermi level. This creates two charge carrier pockets of p type around $\Gamma 2$ and n type around $M 2$, with main components $x^2-y^2$ and (xz, yz). We observe that the Fe–Fe bonding and antibonding bands of xy-character were well separated, lying respectively below and above the Fermi level, and corresponding to configurations $\sigma(b)|^2$ and $\sigma^*(b)^0$. 
Figure 12. Dispersion curves $E(k)$ for the Fe$_2$Se$_2$ unit cell. Red: $xy$ bands separated by a large gap between bonding and antibonding Fe–Fe interactions. Blue: $(x^2−y^2)$ bands, degenerate at the M2 point only. Green: conduction band based essentially on Fe $(xz,yz)$ and Se $4p$ AOs.

The conduction band $σ^*(xz,yz)$ was broad (width > 3 eV); its top was strongly hybridized, with respective weights of 42% and 58% for Fe and Se, and its bottom was mostly of Fe character. It shows a progressive change into a broad domain (ca. 2 eV) with narrower bands built on Fe–Fe interactions. It is close to half-filling, leading to a $(xz)^1(yz)^1$ configuration of Pauli-type states. The two $x^2−y^2$ bands, bonding and antibonding with respect to the Fe–Fe interactions, are noted as $1π_u$ and $1π_g$ respectively. Figure 13 represents a zoomed-in view of Figure 12 around M2 and close to $E_F$, for the six bands arising from $1e_u$, $2e_u$ and $3e_u$, based on $(x^2−y^2/4p_x, 4p_y)$, $(xz, yz)$ and $(xz, yz/4p_z)$ respectively. This corresponds to a $(x^2−y^2)^1$ configuration for Fe.
Figure 13. Enlargement of the dispersion curves of Figure 12, around −12 eV, showing the three bands crossing at M2 ranked by increasing energy: 1π_u/1π_g (1e_u) in blue for x²−y²; 2π_u (not represented)/2π_g (not represented) (3e_u) in green for the xz,yz purely Fe–Fe antibonding interactions, and 3π_u/3π_g (not represented) (3e_u) mixed Se and Fe AOs (in green) with bonding Fe–Fe interactions in the broad conduction band. Note how 1π_g and 1π_u transform respectively in 1σ_u and 2σ_u for the double cell Fe₄Se₄.

Two narrower d² bands are full, for a (z²)² configuration. Overall, this is consistent with divalent Fe, with xy and x²−y² electrons providing the strong cohesion of the network (d_Fe–Fe = 2.67 Å, close to the distance observed in γ-Fe). The hypothesis of a (1π_u)(1π_g) configuration corresponds to a very low U value. Otherwise, the spin polarization of these bands would induce a non-compensation magnetism, as observed in insulating phases of similar structure, with ordered Fe vacancies, such as K₀.₈Fe₁.₆Se₂ (a \sqrt{5} \times a \sqrt{5}, S.G. I₄/m) in which ferromagnetic Fe₄ clusters order in an antiferromagnetic way below ca. 500 K [57].

The occurrence of Fe₄ clusters recalls the O₄ groups in the cuprates discussed above. Furthermore, the low temperature form of FeSe shows an orthorhombic distortion (S.G. Cmna, a/b = 0.9957) whose nematicity arises from the anisotropy of global Fe–Fe nonbonding interactions (antibonding along a, bonding along b) with a a \sqrt{2} superstructure [19,58]. This led us to extend our tight-binding calculations to a double unit cell. The correspondences between crystal orbital notations in the single and double unit cells are given in Table 2. We compare in the following the crystal orbitals of such a double cell for the high temperature P4/nmm and the low temperature Cmna forms, the latter presenting a nematic distortion; we suppose a phonon regime where the parameter ratio a/b oscillates around 1, (1 ± δ).
We focus our attention on the three degenerate crystal orbitals in M₂, i.e., 1eₓ, 2eₓ and 3eₓ at respectively −12.044, −12.035 and −11.986 eV, respectively, and their six split bands towards Γ (note that, for the double cell, x²−y² is transformed into xy): (i) an antibonding-hybridized Fe xy with Se 4pₓ and 4pᵧ AOs in an orbital ordering way, noted as 1eₓ (1πₓ, 1π₀→1σₒ, 2σₒ). Globally, Fe–Fe interactions are NB, the sum of bonding in the a direction and antibonding in the b direction, thus justifying the nematic instability. (ii) A purely Fe, 2eₓ (2πₓ, 2π₀→1πₒ, 2πₒ) band involving equally distributed weights of xz and yz on each Fe atom, arranged in an antibonding manner with the first neighbors and antibonding/bonding ways with the second neighbors. (iii) An antibonding-hybridized Fe–Se, 3eₓ (3πₓ, 3πₒ→3πₒ, 4πₒ) band, involving an orbital ordering, xz for the former and yz for the latter, mixed with Se 4pₓ AOs; each coefficient cᵢ is close for each site. On the basis of degeneracies and regular weight distribution in the various sites, we cannot envisage any tendency of charge fluctuations, quoted here schematically “disproportionation”, cationic and anionic, in the tetragonal phase.

What about the orthorhombic Cmna distortion? For a small iron atom displacement of ± 0.40 pm, the three bands in Γ 4 (= M2) are split by 15, 11 and 25 meV respectively, allowing us to envisage a possible disproportionation.

(i) For the pure iron 2πₒ/2πₘ (2eₓ) bands, we observed an orbital ordering for yz and xz in the two bands; their mixing should only suppressed such an order.

(ii) For the Fe–Se hybridized xy (x²−y²), i.e., the 1σₒ/2σₒ bands, their coefficients cᵢ were equally distributed on each atom (±0.46 for Fe, ±0.17 for Se) conserving an orbital ordering. Distortion and iron oscillation away from their symmetrical positions (phonons), which favored bonding along a (shortest Fe–Fe bonds) in 1σₒ and along b in 2σₒ, changed signs of some AO coefficients. As for the corresponding band of cuprates (Figure 6a), at each half period, the ground state changed from 1σₒ to 2σₒ, violating the NCR of chemistry. To avoid that, the two bands did mix together, progressively up to a complete inversion, with three consequences:

- The creation of an electronic band gap,
- The different sign for the coefficients in the four iron sites between 1σₒ and 2σₒ bands inverted their sum (Σ) or their difference (Δ),
- Passage during this mixture by an appropriate number of pair-occupied states and pair-unoccupied states may induce superconductivity with a 2Δsc gap [23,43].

Using the previous values of cᵢ, we obtained for Σ: c₁ = c₂ = 0; c₃ = c₄ = ± 0.46 for the lower 50:50 mixture (Figure 14), and for Δ: c₁ = c₂ = ± 0.46 and c₃ = c₄ = 0 for the upper one. Two iron atoms out of four carry charge densities on their xy (x²−y²) AOs corresponding to 4(x²−y²)² = 2(x²−y²)² + 2(x²−y²)⁴, or 4Fe²⁺ = 2Fe²⁺ + 2Fe³⁺, qualitatively speaking. Such a succession along [100] and [010] of “Fe” and “Fe³⁺” allows for the Cooper pair formation and condensation at T𝑐 (Figure 15). Such a “disproportionation” is related to the Hubbard parameter U for Fe 3d orbitals and deals also with the difference between the third and the second ionization energies (EL) of Fe, which is the lowest (EL₅ − EL₆ = 14.5 V) value for the M²⁺ 3d transition metal series, as shown in Table 3. However, a similar mixing between Se 4pₓ and 4pᵧ AOs does not show any charge fluctuations in this 1σₒ/2σₒ band.
Figure 14. Orthorhombic Cmma distortion of the tetragonal FeSe double cell showing a nematic distortion along the corresponding phonon mode (see Figure 6), for $1\sigma_u$ ($a/b < 1$ and $B > AB$ on the left) and $2\sigma_u$ ($a/b > 1$ and $B > AB$ on the right), where $B$ and $AB$ represent the strengths of bonding and antibonding, respectively. $1\sigma_u$ and $2\sigma_u$ should mix during this inversion step, when the gap becomes smaller and smaller. The upper part shows the 50:50 mixing; from the AO coefficients in the two bands, two among four Fe atoms do not participate in the mixed wave function. This large charge fluctuation can be schematized as a phonon-induced “disproportionation” state implying electron-pair exchange. As shown in the lower part, the same distortion implies conversely, for $3\pi_u/4\pi_u$ ($3e_u$) mixing, a “disproportionation” state for Se atoms. Note that Se atoms lie above and below the Fe plane (see Figure 11); one layer out of two only contributes to the wave function.
Figure 1. Top: Fe charge disproportionation in the Cmma unit cell of FeSe (Z = 4), by $1\sigma_u-2\sigma_u$ mixing along [100] and [010]. Bottom: charge fluctuation between successive (001) planes of selenium atoms, by $3\pi_u-4\pi_u$ mixing. Fe disproportionation and Se charge fluctuation are both consequences of the noncrossing rule.

Table 3. Values of 2nd and 3rd ionization energies of some transition metals, and their difference (in eV).

|     | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
|-----|-----|-----|-----|-----|-----|-----|-----|
| $E_{I2}$ | 16.49 | 15.64 | 16.19 | 17.08 | 18.17 | 20.29 | 17.96 |
| $E_{I3}$ | 30.96 | 33.67 | 30.65 | 33.50 | 35.19 | 36.84 | 39.72 |
| $E_{I3}-E_{I2}$ | 14.47 | 18.03 | 14.46 | 16.42 | 17.02 | 16.55 | 21.76 |

Besides, the highly split $3e_u$ ($3\pi_u/4\pi_u$) states at the bottom of the wide conduction band with $xz/yz$ orbital ordering (Figure 13) differentiate two out of four selenium positions, above and below the iron layer: $c_1(\Sigma) = -c_2(\Sigma) = 0.20$; $c_3(\Sigma) = c_4(\Sigma) = 0$ and $c_3(\Delta) = c_4(\Delta) = 0$; $c_1(\Delta) = -c_2(\Delta) = 0.20$. Note that these states, upon mixing, do not induce Fe disproportionation.

The Se atoms form a square lattice of $a/\sqrt{2}$ parameter (tetrahedron edge) above and below the iron layer with $\pi$-antibonding Se–Se interactions. At $\Gamma$ point, these interactions add to those of the Fe–Se antibonding character for destabilizing the top of the occupied states, favoring charge transfer. As discussed previously for the cuprates (Figure 8) for the $E(q)$ curve of oxygen, strong similarities were observed for selenium; the created holes can be coupled into pairs and the mixing of the $3\pi_u/4\pi_u$ bands can also contribute to the superconducting gap $2\Delta_c$ (Figure 15). Thus, the Fe–Se system disposed of two, cationic and anionic, phonon coupled carriers for coupling them into pairs and condensing them in Cooper pairs below $T_c$.

Similarly to the case of p-doped cuprates, we examined in which way the Fermi level could shift by a hundred meV to reach the $M_2$ ($x^2-y^2$) point: this would be achieved through an electron transfer from $(x^2-y^2)^*$ to $(xz, yz)^*$ bands, i.e., from $\sigma$ to $\pi$, the latter being more stabilized by the intercalation of cations in the interlayer space, as demonstrated by Pickett and An for MgB$_2$ vs. graphite [59]. The 30 K superconductors $A_{0.6}$FeSe$_2$ ($A = M^+$) illustrated such a behavior, increasing the amount of Fe$^+$ and consequently the Fermi energy, but conversely stabilizing $\pi^*(xz,yz)$ versus $\sigma^*(x^2-y^2)$ as discussed previously [60].
6. Methods

Tight-binding calculations were done using the Extended Hückel method [61–64], as implemented in the CAESAR package [65], using parameters listed in Table 1.

7. Conclusions

The answer to the question in the title is clear: we believe that chemical bonding is at the heart of physical ordering phenomena and contributes to the understanding of the mechanisms of unconventional, high-$T_c$ superconductivity. It sheds light on the key role of nonbonding electrons, from which an electronic instability occurs through a double-well situation, inducing a static or dynamic (phonons) distortion of the atomic network. The coupling of nonbonding electrons with phonons was the core of our chemist’s approach.

At low temperature, the softening of phonons led to a succession of symmetry broken and non-broken states, i.e., the alternation of an insulating distorted phase and a metallic phase. Importantly, it was also at the origin, on a shorter timescale, of a superconducting phase in which the mixing of occupied and unoccupied electron-pair states (described by Wangbo in [23,43]) could be achieved through a purely electronic Hamiltonian. This situation avoids the noncrossing rule for band-edge states, which should swap at each phonon half-period.

Besides, the approach of Micnas et al., based on the mixing of local pairs and itinerant electrons (when wide and narrow bands cross at the Fermi level) giving rise to a mutually induced superconductivity, was also relevant for our model. As discussed recently ([43] and references therein), such an interband electron pairing should also result from the breakdown of the Born–Oppenheimer approximation, favoring interband pair state excitations through nested Fermi surfaces.

The whole scheme applies to the three families of solids discussed here:

(i) Titanates, in which the top of the valence band was nonbonding and induced both a ferroelectric-type distortion, the splitting of the $\pi^*(t_{2g})$ band into a narrow 2D band of $b_{2g}$ symmetry ($xy$) and a broader 2D band of $e_g$ symmetry ($xz, yz$),
(ii) Cuprates (at optimal $p$ doping) had a wide conduction band, of oxygen character and $\sigma^*(b_{1g})$ symmetry, with a 2D Peierls-type instability for nonbonding electrons at the band center. This instability is probably of dynamical nature, and occurred at the Fermi level in the vicinity of a narrow band of pure oxygen character and of $\pi^*(a_{1g})$ symmetry;
(iii) $\beta$-FeSe and iron pnictides of similar crystal structure had a broad conduction band (due to the strong Se (4p)-Fe ($xz, yz$) hybridization) and, close to the Fermi level, a much narrower band of Fe character, likely to split from a nonbonding situation into two bands of $x^2−y^2$ in character, which are Fe–Fe bonding and antibonding, respectively.

In each family, the occurrence of bosonic local pairs was favored by specific features:

(i) A high dielectric constant that minimized the Coulomb repulsion between the two electrons of the $b_{2g}$ local pair ($U→0$),
(ii) The occurrence of a poly-oxide (even peroxide) cluster ($O_2^{−}$), favored both by the almost constant formation energy of the O− ion for charges $q$ between −1 and −1.5, a large transfer integral $t_{O−}$ for hole delocalization, and the local crystal field at the copper-free(+) site, leading to a negative $U$ situation,
(iii) The existence of two ($x^2−y^2$) sub-bands by splitting of 1e$_0$ in Cmma, of nonbonding Fe–Fe character with Fe +II large charge fluctuations, crossing a broad 3D band of ($xz, yz$) character and strongly hybridized with the chalcogen. As in the case of oxygen atoms in the cuprates, the anionic Se layer underwent also similar charge fluctuations, likely coupled together.

These situations agreed perfectly with the requirements of the negative $U$ pairing mechanism, i.e., quasi degenerate states, same coordination and hybridization with the conduction band, as recently reported by Geballe, Hammond and Wu in a general introduction of superconductivity mechanisms [45].
The antagonism between several types of order can be discussed, magnetism vs. superconductivity, and magnetism vs. charge transfer: (i) as well known, magnetism destroys superconductivity above a critical field value, but the magnetic ordering is itself destroyed by charge transfer arising from p-doping in Cu +II cuprates, leading eventually to a collapse of Tc. However, both appear to be at the origin of superconductivity of under-doped cuprates, and their stripe-type insulating phases. (ii) Ferroelectricity and superconductivity seem to be incompatible, despite a few exceptions (see the discussion in Ref. [16]), because a significant carrier density is required (Mott transition). However, studies suggest that ferroelectric-type distortions also induce electron pairing. For both apparent antagonisms, the chemist’ toolbox provides key arguments for possible interpretations.

Finally, the general model proposed here appeared as a coherent mixture of parts of physics and parts of chemistry: (i) the phonon role, alternating broken and unbroken symmetry, (ii) the broad and narrow band crossing of Micnas et al., (iii) the negative U Hubbard model, as ingredients of the BCS theory, for physics, (iv) the non-bonding electron instability, (v) the non-crossing rule of states and bands and (vi) the charge-transfer disproportionation (which is equivalent to negative U), for chemistry. In addition, chemistry also suggests that anionic hybridization like Os±3 Os±5 AOs, rejecting alternatively electron densities on both sides from the symmetry center, describes very well the atomic polarizability and could be a high frequency alternative to phonons. In addition, coupling cationic and anionic disproportionation could enhance superconductivity as observed in cuprates and selenides.

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