Pb-apatite framework as a generator of novel flat-band CuO based physics, including possible room temperature superconductivity.

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Abstract:

Here, based upon density functional theory (DFT) calculations, we present the basic electronic structure of $CuPb_9(PO_4)_6O$ (Cu-doped lead apatite), showing that the low energy (near-Fermi level) states are dominated by Cu-O hybrid states. The filling of these states is nominally d^9, consistent with the standard Cu^{2+} valence state. We find these states to be unusually flat (~ 0.2 eV dispersion), giving a very high density of electronic states (DOS) at the Fermi level that we argue can be a host for novel electronic physics, including potentially room temperature superconductivity. The states are in general sensitive to symmetry-lowering gapping possibilities that would remove the spectral weight from E_F, but could be protected from this by disorder/doping heterogeneity in a real material. Importantly, this disorder is expected to be less damaging to superconductivity. Further, we claim that the emergence of these flat bands should be due to weak wavefunction overlap between the orbitals on Cu and O sites, owing to to the directional character of the constituent orbitals. Therefore, finding an appropriate host structure for minimizing hybridization between Cu and O while allowing them to still weakly interact should be a promising route for generating flat bands at E_F and very high temperature superconductivity, regardless of whether "LK-99" is such a realization.

Introduction:

A brand-new potential superconductor with chemical formula $Cu_xPb_{10-x}(PO_4)_6O$ $0.9<x<1.1$ named "LK-99" was recently reported [1,2] claiming to be the world's first ambient pressure room-temperature superconductor. In particular, many signatures of superconductivity were found to exist up to 400K (127 C), including diamagnetic responses and strong reductions in electrical resistance. And while skepticism as to the validity of the claims of superconductivity is strong and will likely exist at least until the experimental findings are verified by a few other groups, here we show that the electronic structure of this class of compounds is very interesting in its own right, and has many features expected to be supportive of superconductivity at very high temperatures. In particular, we show that the process of doping Cu atoms on the particular Pb(4*f*) site described in [1,2] generates a pair of electronic bands of approximately equal Cu (t_{2g}) and O (p) character that exist at the Fermi level of the new compound, with these bands having an especially small bandwidth of order 0.2 eV . It is noteworthy that the Cu character near E_F consists only of a single state, a particular linear combination of three t_{2g} that if the symmetry were cubic, would be three-fold degenerate. In this case the crystal field splits the t_{2g} so that only one Cu-derived orbital remains near E_F. Finally, this remaining t_{2g} state lies above the e_g state, reversed from the cuprates.

Experience with many other electronic compounds with flat electronic bands right at the Fermi level immediately signals the possibility of exotic properties as such states tend to be extremely "active". That is, the high density of electronic states at E_F that comes with these flat bands tends to lead to electronic instabilities of various kinds, including density wave instabilities and/or superconductivity. Also helpful for generating exotic properties are systems with small spin magnetic moments as these usually bring strong quantum fluctuations of the spins. A good example is the Cu-O based "cuprate" high temperature superconductors [3] with spin ½ moments on the Cu sites, or more specifically, partially delocalized across Cu-O clusters [4]. We find that the present system also should contain spin-1/2 moments associated with Cu, consistent with the d^9 (Cu 2+) valence state that our calculations show.

We will argue that these flat CuO derived bands do not occur by accident in $Cu_xPb_{10-x}(PO_4)_6O$ $0.9<x<1.1$, but rather should be due to minimal direct coupling between the Cu 3d and O 2p wavefunctions. (Already in the parent compound, the band dispersion of the O-derived valence band maximum itself has narrow dispersion.) This reduced coupling gives a reduced E vs. k band dispersion (flat bands) and an associated high electronic density of states. We find a portion of these flat bands/ high density of states live right at E_F so they should become strongly electronically "active" – potentially generating superconductivity at very high temperatures through one of many possible channels, as will be discussed later. If superconductivity does indeed exist in LK-99, our results imply that it is enabled by the ultra-flat CuO bands at E_F. If it does not exist in LK-99, we suggest that the concepts outlined here can be used as guidance for finding other possible hosts besides Pb apatite that generate electronically active flat bands at E_F.

Fig 1 shows a schematic of how to obtain ultraflat bands, as illustrated for Cu (red) and O(blue) hybridized wavefunctions. Panel (a) is illustrative of "native" Cu-O bonds, where the wavefunction overlap is large In this case (as occurs in the cuprates) Cu and O form strong covalent bonds. which gives rise to a significant dispersive bandwidth W_0. (Panel b) -The phosphate (PO_4 unit) indeed forms strong covalent bonds: mutually directed sp^3 hybrids on P coupled to O p states oriented at the P, form a strong two-center bond. These states are far from the Fermi level. For strong covalent Cu-O bands to form, there must be similar overlap between the Cu d and the remaining O p orbital orthogonal to the one oriented to P. If the directionality of the available bond orbitals precludes strong overlap, the hybridization will be weak and the band dispersion is

small. This appears to be the case for apatite structure, in both the parent compound and the Cu-doped one.

Absent some symmetry breaking, we can expect the system doped the (insulating) parent compound and be metallic with one hole. In a metal with very flat bands bands at E_F, the system will find some way to lower the symmetry and open gaps. The flatter the bands get, the greater the driving force to gap the bands at E_F. There are many possibilities, including structural relaxation that breaks the P3 symmetry (see below); with this symmetry-lowering gapping strongly competing with superconductivity, as the superconductivity requires these low energy ungapped states. Panel (f) illustrates how small amounts of random disorder, for example from incommensurate doping levels (x not equal to 1) or doping onto different nominally equivalent sites, can protect the flat bands from such gapping effects, keeping them available to support high temperature superconductivity. We note that this system, owing to its weak hybridization, may be more sensitive to disorder than established superconductors. In this regard we note that non-sign changing s-wave superconductivity should generally be robust against the same disorder that can be used to protect the flat bands from other gapping mechanisms, as first shown by Anderson [5].

These ingredients are different from those proposed in refs [1,2] for the superconductivity. In their case, they argue that the relevant states for the superconductivity are $6s^1$ states from the six-fold degenerate Pb atoms (which we call Pb(6)) with these states affected by the compressive strain of the inserted Cu atoms, leading to an insulator to metal transition and setting the stage for superconductivity. Our electronic structure calculations show negligible amounts of Pb 6s spectral weight near the Fermi level, which are dwarfed by the density of states contributions from the Cu3d and O2p atoms. Therefore, if there is superconductivity in this system, it should be from the Cu and O states that are held in place by the Pb apartite lattice, rather than by the effect of the Cu on the Pb states in the apartite lattice.

Following this introduction, we present the details of our electronic structure calculations, beginning with the structures that these calculations are based upon.

Crystal structures of $Pb_{10}(PO_4)_6O$ and $CuPb_9(PO_4)_6O$:

We note from the outset that the physical structure of $CuPb_9(PO_4)_6O$ (or the LK-99 materials) hasn't yet been fully determined, with this information needed to make the most accurate electronic structure calculations. When that structural information becomes available, finer details of the electronic structure will be able to be determined – until then, we believe that the present results can help give a first-order understanding of the novel electronic states that should exist in this compound.

The "parent" compound of the material under consideration is the Pb apatite $Pb_{10}(PO_4)_6O$. This compound had been previously synthesized in single crystalline form 20 years ago, with detailed structural characterizations from X-ray diffraction measurements performed on these crystals [6], including a .CIF structure file that is available in the ICSD database. This structure belongs to the P63/m hexagonal symmetry class (number 176) and consists of four Pb(4f) and six Pb(6h) sites, six PO_4 tetrahedra each containing an O(1), O(2), and O(3) site, as well as four O(4) sites that are each ¼ occupied. To avoid inconsistencies found in the literature we use Wykoff notation and refer to the four equivalent Pb atoms as 4*f*.and the remaining symmetry-equivalent Pb atoms as 4*h*. We also note that the ¼ occupation of the four O(4) sites implies that the description of the structure as a long-range ordered state is imperfect, implying some local distortions that were not captured in the structure files. To deal with the ¼ occupation in our electronic structure calculations we made the approximation that one of the four O(4) states should

be occupied while the other three are not. The choice of which of the O(4) sites to put the oxygen in is irrelevant at this stage, as long as the same choice is maintained for all cells in a bulk crystal, i.e. perfect oxygen ordering – something that is unlikely and probably related to (or causing) the local distortions discussed above.

References [1] and [2] indicate the composition of the new superconductor as $Cu_xPb_{10-x}(PO_4)_6O$ with $0.9<x<1.1$ so we choose $x=1$, i.e. $CuPb_9(PO_4)_6O$. Reference [2] states that the Cu replaces one of the four Pb(4f) atoms. We built our cell this way and illustrate it in Fig 2b, which shows a top view projection of $CuPb_9(PO_4)_6O$ focusing on the Cu sites (red) which are substituted on ¼ (~ ½ in this view) of the four-fold Pb(4f) sites (yellow), the blue O(4) atoms, and the six-fold Pb(6h) (green). The hashed triangles indicate the PO_4 tetragons, which form strong two-center bonds as noted above, and are electronically inactive at the. Fermi level. Also shown at the bottom right is one example of doping disorder, where the Cu goes into the "wrong" Pb(4f) site. Figure 2c shows a three-dimensional view of the $CuPb_9(PO_4)_6O$ structure.

Reference [2] also indicates that compared to the parent compound the in-plane lattice constant a shrinks from 9.865 Å to 9.843 Å while the out-of-plane lattice constant c shrinks from 7.431 Å to 7.428 Å, i.e. an overall volume shrinkage of 0.48 We determined the lattice vectors by minimizing total energy with the SCAN functional (see below)

Calculational methods:

Total energy and atomic relaxations were calculated within density functional theory (DFT) at the levels of the generalized gradient approximation (GGA) [7], GGA+U [8], with U_{Cu-d} = 5 eV, and the SCAN meta-GGA [9] using the projector augmented wave approach implemented in the VASP code [10]. All three functionals yield broadly similar results. The atomic structure models were constructed starting from the experimental refinement of $Pb_{10}(PO_4)_6O$ [11] in the $P6_3/m$ (#176) space group, as given in the Inorganic Crystal Structure Database (#98703), with a 41 atom primitive cell for one formula unit (fu). This is a disordered structure with ¼ occupancy on the O4 (4e) site. To maintain the 41 atom cell size, we selected one of the 4 sites to be occupied and the remaining 3 sites to be empty, which induces pronounced local geometry changes compared to the average structure of the disordered phase. (Note that the local structure is typically not resolved in diffraction experiments.) Within this cell, the subsequent Cu substitution on the Pb(4) site [2] of the original structure leads to 4 different configurations, with 2 pairs of almost identical total energies, as summarized in Table I. These results were obtained from collinear spin-polarized calculations using a 2×2×4 k-mesh for Brillouin sampling and including relaxation of atomic forces and cell volume and shape with a stopping criterion of 0.03 eV/Å.

The Cu-O configurations within the 41 atom simulation cell, obtained after atomic substitution, are ordered with a resulting $P3$ (#143) space group symmetry. Preserving this symmetry in the charge density, the system becomes a half-metal with a total spin moment of 1 μ_B, at the PBE level. However, when allowing for electronic and atomic symmetry breaking, an energy gap opens at E_F (see Table I), consistent with Cu^{2+} in a d^9 configuration. Interestingly, this solution, without remaining space group symmetries, is stable even in standard DFT at the GGA level (Table I), despite the well-known failure to open a gap, e.g., in CuO [12].

The gap opening in the symmetry-broken configuration should be facilitated by the small unit cell with its implied atomic and electronic (spin and orbital) ordering, and it would likely be weakened in the presence of disorder. Fully accounting for disorder in an atomistic model without fractional occupancies would require configuration sampling in larger supercells, including both atomic (here, Cu_{Pb2} and O_{O4}) and electronic degrees of freedom. Monte-Carlo (MC) simulations

of disorder have long been the domain of model Hamiltonian approaches like cluster expansion [13,14], especially for combined sampling of atomic and magnetic configuration [15,16], but DFT based first-principles MC simulation are becoming increasingly feasible and effective [17]. However, for the purpose of the present preliminary work, we will consider the results obtained within a single 41 atom primitive cell without and with symmetry constraints.

Results: Band structure of $CuPb_9(PO_4)_6O$.

Fig 3 shows the calculated density of states of $CuPb_9(PO_4)_6O$ calculated with the GGA PBE functional and U=5 eV at the Cu site. A narrow (< 0.2 eV) set of bands of dominant CuO origin appears at E_F, with no gap, indicative of a metallic state. The electron count is near d^9, similar to the cuprate superconductors. For these calculations we allowed the structure to relax while preserving the original P63/m symmetry of the starting structure, which preserved the metallic state. If we allow the symmetry to be further lowered, a gap will open at the Fermi level, producing an insulator (see table 1).

Figure 4 shows the E vs. k band dispersion from the same symmetry-protected calculation. We again see the narrow set of CuO derived bands at E_F, which are split off from the bands slightly below. The bands are differentiated by their spin direction, with the Fermi energy in the down-spin manifold of states. Table 2 shows the magnetic moments extracted from our calculations. These were single unit cell calculations without spin-orbit interactions, so the moments are colinear. We started the calculations with a magnetic moment of 1 mu_B on each Cu site and let the moments evolve as the self-consistent loop converged. The table shows that the majority (96%) of the spin remains, i.e. it is close to spin 1/2. Interestingly, just under half of the moment remains on the Cu site with the remainder spread among the many hybridizing O atoms.

Figure 5 shows projections of the calculated bands onto the various Cu d-orbital symmetries. We find the the d_{xy}, d_{xz}, and d_{yz} states all have significant spectral weight at E_F, in strong contrast to conventional cuprate superconductors where the bands at E_F are d_{x2-y2} derived. This difference has to do with the local bonding directionality between the Cu and O atoms, though it isn't clear yet what impact, if any, this might have on superconductivity.

Discussion and implications.

Our finding, through calculation, of flat CuO bands at E_F in Cu-doped Pb apatite is generally consistent with the statement in [1,2] that this kind of system can (or may be) supporting superconductivity to very high temperatures. This is because such flat bands and their associated high density of states are generally strongly favorable for superconductivity, which in BCS theory exponentially varies with the density of states at E_F. That is, a host of nearly degenerate electrons, with high density of states over the entire Brillouin zone might significantly gain energy by pairing up and gapping out the Fermi surface, i.e. creating a superconducting phase. However, it does not eliminate the possibility for the system to choose some magnetic or charge ordered phases that will compete for those same states, lowering or fully quenching the superconductivity. It requires a more careful analysis of all possible competing instability-channels to explore what the material chooses as its ordered ground state. Extremely flat states at the Fermi energy can also significantly enhance the electron-phonon coupling matrix elements, which would also support higher

superconducting transition temperatures. In contrast with the hydride superconductors, the phonon modes are less violent for oxygen and copper and may not need high pressures to prevent the system from falling apart. The presence of disorder and flat electronic states together suggest the material may choose an s-wave superconducting phase. Most importantly, the Cooper pairing in that case will probably be better described by a strong coupling picture akin to the BEC limit where Tc/T_F > 1/10.

To summarize, we turn to Figure 1. We have established that the weak hybridization and flat bands can lead to instabilities of different kinds (a) and (b). It remains for future work (Figures (c) and (d)) to compare possible competing phases.

Note added: A similar work done simultaneously as ours has just appeared on the arXiv [18].

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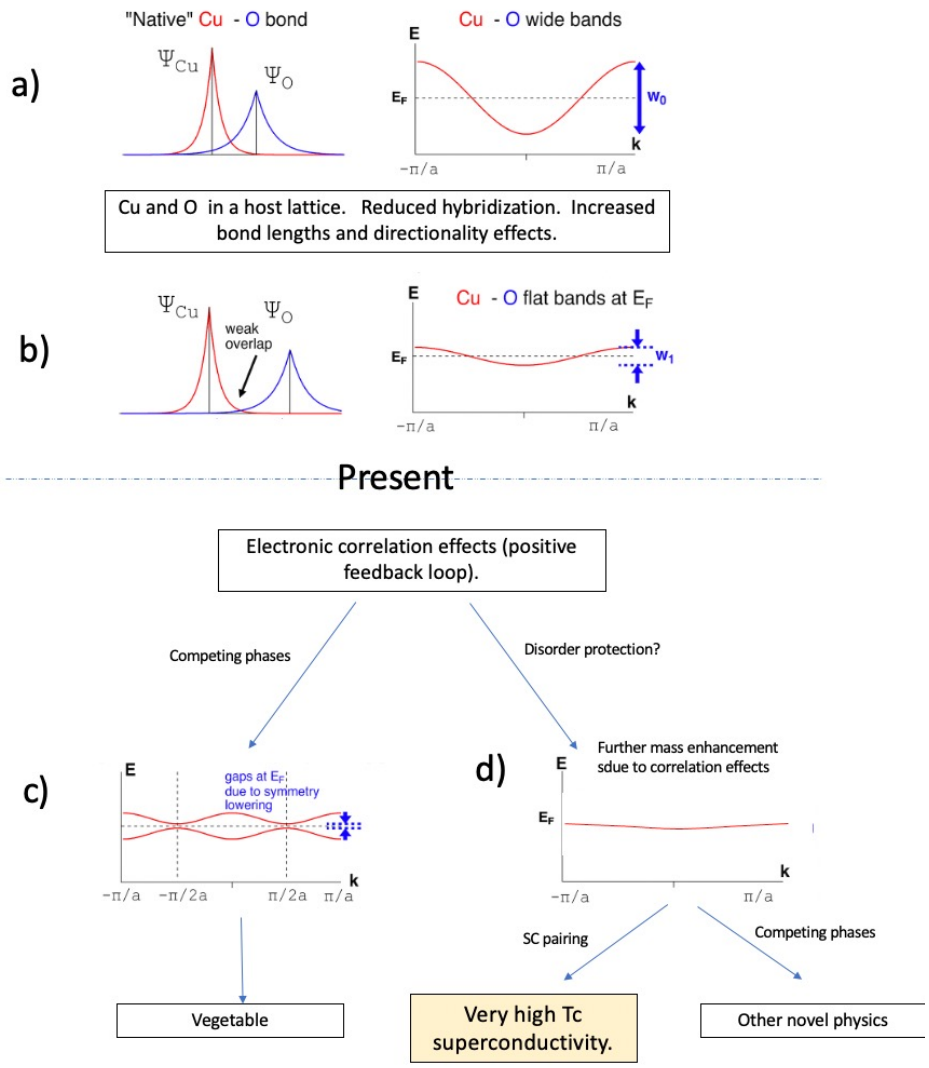

Fig 1. Roadmap for obtaining strongly renormalized ultraflat CuO bands in a host lattice, potentially leading to very high temperature superconductivity. Our calculations show that we are in between steps b and c.

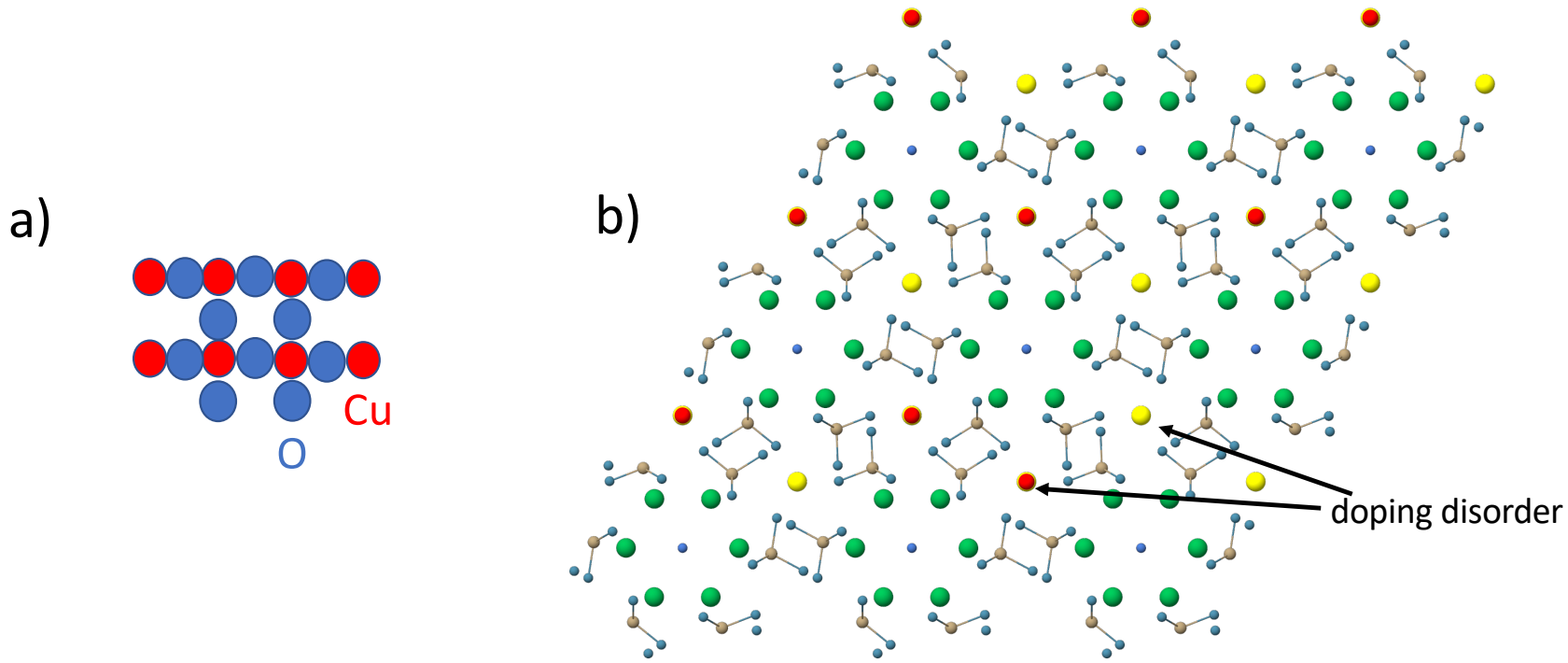

Fig 2. a) Natural bond distances betwnee Cu and O in a CuO lattice, give a large bandwidth W_0. b) Top view projection of $CuPb_9(PO_4)_6O$ focusing on the Cu sites (red) which are substituted on ¼ (~ ½ in this view) of the four-fold Pb(4f) sites (yellow), the blue O(4) atoms that will hybridize with the red coppers, and the six fold Pb(6h) (green). Also shown at the bottom right is one example of doping disorder, where the Cu goes into the "wrong" Pb(4) site.

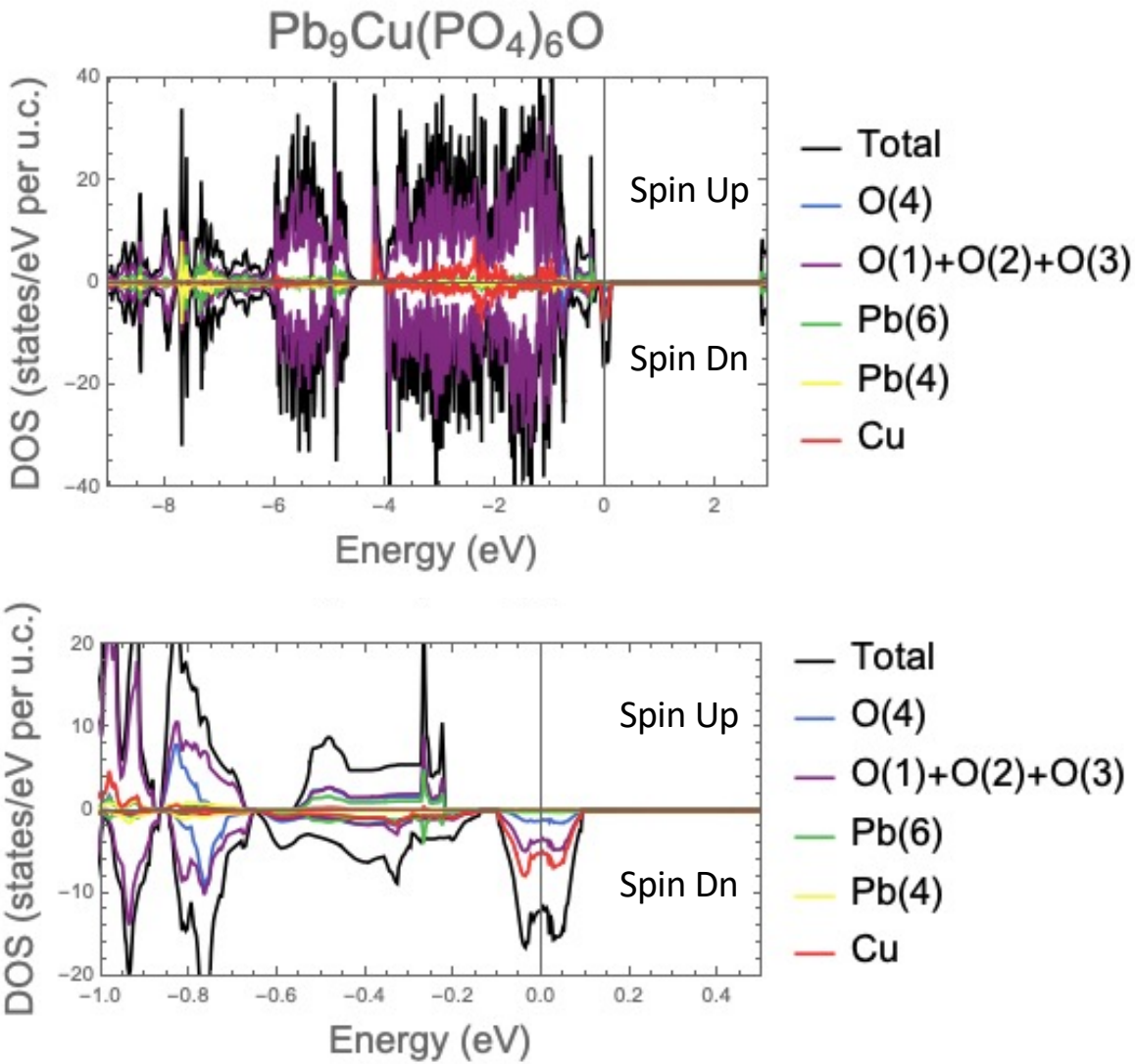

Fig 3. Density of states of $CuPb_9(PO_4)_6O$ calculated with the GGA PBE functional and U=5 eV at the Cu site. A narrow set of bands of dominant CuO origin appears at E_F, with no gap indicative of a metallic state. The electron count is near d^9, similar to the cuprate superconductors. We allowed the structure to relaxwhile preserving the original P63/m symmetry of the starting structure. If we allow the symmetry to be lowered a gap will open at the Fermi level, producing an insulator (see table 1).

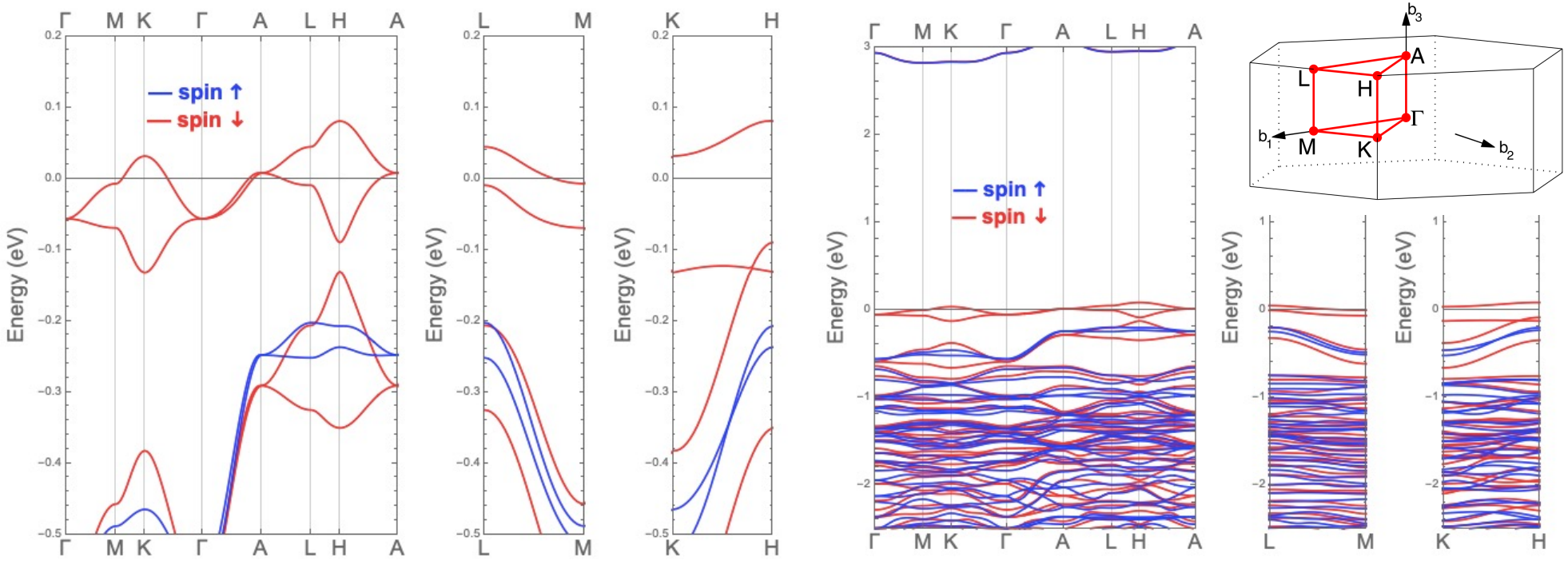

Fig 4. The band structure of $CuPb_9(PO_4)_6O$ associated with the DOS of Fig 3.

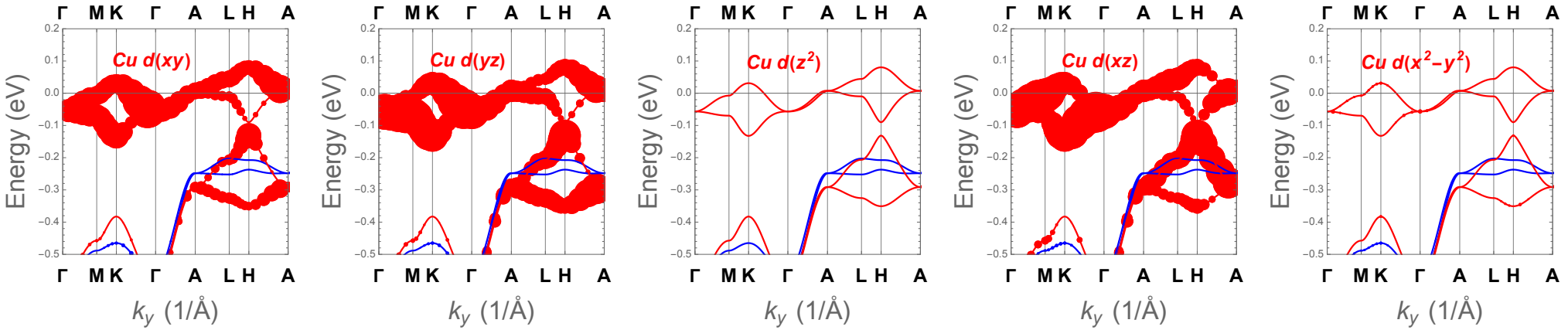

Fig 5. Orbital projections of the flat bands at E_F in $CuPb_9(PO_4)_6O$, with spectral weight indicated by the size of the circles. In contrast to standard cuprate superconductors which have the near EF weight from x2-y2 orbitals, the weigt here is from the Xy, xz, and yz orbitals.

Functional	Cu-O configuration	symmetry preserved (eV/fu)	symmetry broken (eV/fu)	energy gap symmetry broken (eV)
GGA	1	0.41	0 (lowest state)	0.56
	2	0.65	0.08	0.46
GGA+U	1	0.83	0 (lowest state)	1.22
	2	1.23	0.08	1.12
SCAN	1	0.46	0 (lowest state)	1.31
	2	1.04	0.27	1.20

Table 1: Relative energies (eV/fu) of the two Cu-O configurations in the three different functionals, comparing calculations preserving and breaking the initial space group symmetry of the atomic configuration. The symmetry-preserved structure is metallic, and the energy gap of the symmetry broken phase is given in the table.

atom/site	moment (μ_B)
O(4)	0.131
O(1)+O(2)+O(3)	0.342
Pb(1)	0.053
Pb(2)	0.
P	-0.003
Cu	0.442
Total	0.965

Table 2: Magnetic moments of $CuPb_9(PO_4)_6O$ calculated with the GGA PBE functional and U=5 eV at the Cu site, as in Fig 3 and 4. Approximately half of the moments are distributed among the hybridizing O atoms.