Comment on “Apical Charge Flux-Modulated In-Plane Transport Properties of Cuprate Superconductors”

The abstract of Ref. [1] claims to “demonstrate, using *ab initio* computations, a new trend suggesting that the cuprates with stronger out-of-CuO₂-plane chemical bonding between the apical anion (O, Cl) and apical cation (e.g., La, Hg, Bi, Tl) are generally correlated with higher $T_{c,\max}$ in experiments.” We point out that this trend is *included* in the long-known [2] correlation of $T_{c,\max}$ with the hopping range ($\sim t'/t$) of the electrons at (the most interlayer-bonding sheet of) the Fermi surface. Contrary to the impression given in Ref. [1], the correlation [2] is not simply with the distance d_A of apical oxygen from the nearest CuO₂ plane; but rather, as stated in the abstract of Ref. [2], “It is controlled by the energy of the axial orbital, a hybrid between Cu 4s, apical-oxygen 2p_z, and farther orbitals.” The bonding between the apical cation (AC) and apical anion (AA) describing $T_{c,\max}$ in Ref. [1] is included in the energy of the axial orbital illustrated in Fig. 3 of Ref. [2].

The axial orbital (s), is the 4th orbital which must be added to the 1st near-neighbor (1 nn) three-band CuO₂ model, parametrized by ϵ_d , ϵ_p , and t_{pd} , to define a four-band model with two additional parameters: the energy ϵ_s of the axial orbital and its hopping integral t_{sp} to a nn oxygen in the CuO₂ plane (Fig. 1 in Ref. [2]). The axial orbital is the vehicle for hopping around a corner of the square Cu lattice, a hopping which in the 2 nn three-band model is described by $t_{pp} = t_{sp}^2/(\epsilon_s - \epsilon_F)$, and in the one-band model by $t' \approx rt$. Here, $r = 2t_{pp}/(\epsilon_F - \epsilon_p + 4t_{pp})$ is the range parameter. Of the 1 nn four-band model’s five parameters, *only* ϵ_s was found to vary significantly among materials. Hence, the most microscopic parameter found to correlate positively with $T_{c,\max}$ was the inverse of the excitation energy $\epsilon_s - \epsilon_F$ for hopping around a corner.

Equation (3), with t_{pz^2} neglected for simplicity, plus the two following lines in Ref. [2] give the energy of the axial orbital as

$$\epsilon_s = \epsilon_{\text{Cu}4s} + \frac{2t_{\text{AA,Cu}4s}^2}{\epsilon_{\text{Cu}4s} - (\epsilon_{\text{AA}} - \frac{t_{\text{AA,AC}}^2}{\epsilon_{\text{AC}} - \epsilon_{\text{AA}}})} \quad (1)$$

in terms of the energies, $\epsilon_{\text{AA}} < \epsilon_F < \epsilon_{\text{Cu}4s} < \epsilon_{\text{AC}}$, of, and hopping integrals, $t_{\text{AA,Cu}4s}$ and $t_{\text{AA,AC}}$, between its atomic constituents. It expresses that the energy ϵ_{AA} of apical-oxygen 2p_z is *lowered* due to the repulsion from the AC orbital (e.g., La 5d_{3z²-1} or Tl 6p_z) and that the energy of

Cu 4s is *raised* due to the repulsion from apical-oxygen 2p_z. The bonding between AA and AC, demonstrated in Ref. [1] to correlate positively with $T_{c,\max}$, is essentially the amount $t_{\text{AA,AC}}^2/(\epsilon_{\text{AC}} - \epsilon_{\text{AA}})$ by which the denominator in Eq. (1) is increased due to this bond. This, in turn, is seen to cause the energy of the axial orbital to decrease towards that of the bare Cu 4s and, hence, according to Ref. [2] be associated with a higher $T_{c,\max}$; Q.E.D. In the words of Ref. [1]: “... the closer the hybridization peak is to the Fermi level (ϵ_F), the higher the $T_{c,\max}$ is.”

Equation (1) also exhibits causes for an increased $T_{c,\max}$ not captured by Ref. [1]. For instance, increasing the distance d_A to AA, thus *decreasing* the AA–AC distance, causes not only an increase of $t_{\text{AA,AC}}^2$, but also a *decrease* of $t_{\text{AA,Cu}4s}^2$, and thereby leads to an even stronger decrease of ϵ_s towards $\epsilon_{\text{Cu}4s}$ and, hence, an even stronger increase of $T_{c,\max}$. That $T_{c,\max}$ generally increases with d_A is, however, *not* true, because also ϵ_{AA} and ϵ_{AC} (the nature of AA and AC) matter, unless d_A is so large that $t_{\text{AA,Cu}4s}^2 \sim 0$ (almost the case of Tl and Hg in Fig. 4 of Ref. [2]).

Most importantly, whereas the correlation [2] extends in a straightforward way to the numerous higher- T_c bi- and trilayer cuprates, the correlation [1] does *not*, simply because the bonds between AA and AC are *outside* the multilayer. Instead, Ref. [1] ascribes the observed trend to charge transfer from a vertically vibrating AA to a CuO₂ layer, i.e., a higher-order dynamical process, but fails to make this mechanism plausible by applying it to several materials and produce a figure like Fig. 5 in Ref. [2] or Fig. 1 in Ref. [1].

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