Van Hove Singularities around the Fermi level in YBa$_2$Cu$_3$O$_7$: The importance of the chains.

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Abstract

We have reproduced band structure calculations from the literature and have used them to analyze in detail the energy landscape around the Fermi level, $E_F$. We found three Van Hove singularities, two below (-230, -54 meV) and one above the Fermi level (+27 meV). We have studied the composition of each one of them and found that states coming from the chain do contribute in a very important way. The contribution from the planes are indeed important and, therefore, we find that a 2D description includes the most important contributions. Nevertheless, the contribution from states out of the planes (the chains and the apical oxygen) is by no means negligible. We find that it is possible that in YBaCuO part of the condensate lies in the chains, a fact that would agree with some recent evidences concerning PrBaCuO. Our general conclusion is that the 2D description of 123-compounds might be insufficient to explain all the experimental details and that a 3D description seems compulsory to fully account for the phenomenon of superconductivity in YBaCuO.

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I. INTRODUCTION

In a recent paper, Quesada et al. have reviewed the thermodynamics of YBa$_2$Cu$_3$O$_7$ within the van Hove scenario. We find that it explains a number of experiments, as Bok and Bouvier have stated recently. Nevertheless, some of the results deviate from the experimental ones, sometimes considerably. The inclusion of other scenarios as active in the superconducting state could bring more light into the problem, first, because the three-dimensional dispersion (c-axis) can be important as Pickett et al. have suggested, and secondly, because the condensate might lie (at least in part) in the chains. Indeed, Cucolo et al. made a simulation of their experimental results for YBa$_2$Cu$_3$O$_7$ (tunneling, specific heat and ultrasonic attenuation) where they have included the CuO$_2$ planes, the b-axis CuO chains and the c-axis as active scenarios. Their description of each scenario is particularly simple and still the three experiment are brought into agreement. For superconducting PrBa$_2$Cu$_3$O$_7$,
Dow and Blackstead\cite{6} reported, very recently, experimental results and interpreted them as demonstrating that the condensate lies in the chains.

In this paper, we show that the CuO chains parallel to the b-axis could also play a role in superconducting YBa$_2$Cu$_3$O$_7$. We analyzed in detail the 3D density of states around the Fermi level, $E_F$, and found three Van Hove singularities, two below at -230 and -54 meV, respectively, and a third one above $E_F$ at +27 meV. To this end, we have located in the 3D E vs. $k$ space, the corresponding saddle points that produce them. Most importantly, we show that the highest contribution to the nearest below-$E_F$ Van Hove singularity comes from chain states. There is no consensus about the role that the Van Hove singularities play in the superconductivity of high-T$_C$ superconductors (HTSC)\cite{6} but if they play any at all, then our result shows that the b-axis CuO chains have to be taken into account for a proper description of superconductivity in YBa$_2$Cu$_3$O$_7$. Andersen et al.\cite{6} stressed long ago the importance of saddle points very close to the Fermi level. More generally, the composition of the Density of States (DOS) in the vicinity of the Fermi energy, indicates that a 2D description of YBa$_2$Cu$_3$O$_7$ could turn out to be insufficient. Pickett et al.\cite{7} emphasized that the c-axis dispersion will lead to apparent broadening of the Fermi surface in experiments interpreted in terms of a 2D electronic structure. Also Schuller et al. found in an early series of experiments\cite{8} that the chains play an important role in YBa$_2$Cu$_3$O$_7-\partial$.

The rest of the paper is organized as follows. In section 2, we describe in detail the three Van Hove singularities that we found. In section 3, we analyze their composition and the one around $E_F$. Section 4 is devoted to our conclusions.

II. THE VAN HOVE SINGULARITIES

We have reproduced the band structure calculations of DeWeert et al.\cite{3} for YBa$_2$Cu$_3$O$_7$. We use their tight-binding version. A certain precision is lost but the essential idea will not change at all. Since these authors have carefully fitted their \textit{ab initio} bands near the Fermi level, the loss of precision is diminished. We gain, in exchange, a very quick way of reproducing parts of the energy landscape to analyze in detail. We have calculated an important number of them to find the location of the saddle points that produce the Van Hove singularities.

In Fig. 1, we show the Density of States (DOS) about 0.8 eV around the Fermi level where one expects the most important states that participate in building the condensate, to lie. The origin is at $E_F$. In this range of energy, we found three Van Hove singularities which we have labelled vHs$_1$, vHs$_2$ and VHS$_3$. We find VHS$_1$ at -230 meV. It is located at $k_1=(0.42\ \pi/\ a, \ 0.13\ \pi/\ b, \ 0)$. VHS$_2$ is at -54 meV at the high-symmetry point $Y=k_2=(0, \ \pi/\ b, \ 0)$. Finally, we found VHS$_3$ above $E_F$, at +27 meV. This one is located at $k_3=(0, \ \pi/\ 2b, \ 0)$. The axes are labelled $a$, $b$, $c$ as it is conventional.

Notice the high peak at about -200 meV. It comes from a maximum in the 3D E vs. $k$ space. None of the singularities appears to be at an important maximum in the DOS. Only vHs$_3$ is located at a small maximum. One of the ideas behind the Van Hove scenario formulation is that the DOS would be incremented in an important way by the presence of a singularity in the vicinity of $E_F$. The 3D DOS does not seem to support this idea.
We found the Van Hove singularities by looking at the energy landscape in the first Brillouin zone (FBZ) for energies above and below $E_F$. We identified the saddle point that produces each Van Hove singularity from 3D color plots of the energy landscape (not reproduced in this paper). To check the saddle point, we calculated the band structure in different paths passing through it and confirmed that we had a maximum in some direction and a minimum in the perpendicular one.

In Fig. 2a, we locate VH$s_1$. The upper part shows the band structure from $(\frac{7\pi}{20a}, 0, 0)$ to $(\frac{2\pi}{2a}, \frac{3\pi}{50b}, 0)$. We indicate the band at the point it has a minimum. In the lower part, the band structure appears from $(0, \frac{\pi}{4b}, 0)$ to $(\frac{17\pi}{20b}, 0, 0)$. The arrow indicates the place where the maximum appears. The two paths cross at $k_1$. In 3D, a saddle point is formed. The energy at which the saddle point is formed is $-230$ meV.

Fig. 2b, we repeat the procedure for VH$s_2$. It is the nearest-to-the-Fermi-level Van Hove singularity below $E_F$. It is located at $-54$ meV. It is quite near $E_F$. These states are occupied in the normal state and should participate in the formation of the superconducting condensate. For that reason this singularity might play a role.

In the upper part of Fig. 2b, we can see that this band has a minimum in the $(\frac{\pi}{a}, \frac{\pi}{b}, 0)$ direction and a maximum in the perpendicular one from $(0, \frac{\pi}{b}, 0)$ to $(0, \frac{3\pi}{2b}, 0)$. The saddle point is at the high symmetry point $Y = k_2 = (0, \frac{\pi}{b}, 0)$. In 3D it forms a saddle point. The corresponding energy is $-54$ meV.

For the case of VH$s_3$, we have produced Fig. 2c. In this case, we show, in the upper part of the figure, a path from the center of the FBZ, $\Gamma = (0,0,0)$ to $(0, \frac{\pi}{b}, 0)$. Here again the arrow points to the maximum that identifies the saddle point in this case. The lower part illustrates the minimum. The paths cross at $k_3 = (0, \frac{\pi}{b}, 0)$. The corresponding energy is at $+27$ meV. It is located just above the Fermi level and it is possible that some electrons are promoted here in the superconducting state since YBa$_2$Cu$_3$O$_7$ has a critical temperature, $T_c$, of about 100K. Summarizing the results of this section, we found three Van Hove singularities in the vicinity of $E_F$. Two of them are very close to it. One below (vH$s_2$ at $-54$ meV) and one above (vH$s_3$ at $27$ meV). These could play a role since the states in the first should participate in the formation of the condensate and some electrons could be promoted to the one next section we will study the composition of these singularities.

III. ANALYSIS OF THE COMPOSITION.

A very interesting point to look at is the composition, i.e., the states that contribute to the DOS at each Van Hove singularity. We show this result in Fig. 3 where we draw explicitly the contribution that we get from the different states around the Fermi level. The energy at which the Van Hove singularities appear and the Fermi level, $E_F$, are shown. We present three set of data. The scales are the same. The upper part is devoted to the contribution coming from the b-axis CuO chains composed by the atoms labelled Cu(1) and O(1), as it is conventional. In the middle part, we show the contributions coming from the CuO$_2$ planes. These atoms are labelled Cu(2), O(2) and O(3). In the bottom part of Fig. 3, the contributions from the apical oxygen O(4) and from the Y atom are shown. These contributions are calculated here per atom, not per unit cell. We will do that below. Around $E_F$, the Y-contribution is negligible.
The contribution to the DOS from atoms belonging to the chain, Cu(1) and O(1) are roughly of the same size, in the interval around $E_F$ that we are considering, although the one from Cu(1) seems to be always slightly higher than the one coming from O(1) (see upper part). In the middle part of the figure, the corresponding contribution from the atoms that belong to the planes, for energies in the interval from about -250 meV to $E_F$, differ strongly. The Cu(2) and O(2) (on the a-axis) atoms, both contribute about the same and their contribution is comparable to the chain atoms, in this interval of energy. On the contrary, the states associated to the O(3) atom (on the b-axis, where the chains lie as well) contribute only about one half as compared to the former ones. In the lower part of Fig. 3, we can see the important contribution to the DOS at the energies that we are considering that comes from the apical atom O(4).

A high peak at about -200 meV is composed mainly of states that come from O(1) and C(1), the b-chain atoms, and from the O(4) apical atom. At this energy we find a maximum in the E vs. k space not a VHs. These states could take part in the formation of the condensate and, more generally, in the thermodynamics of the superconducting state but they are not included in a 2D formulation.

Let us concentrate now on the singularities. We see from Fig 3 that at VHs$_1$ (-230 meV) the contributions from chain atoms Cu(1) and O(1), from the plane atoms Cu(2) and O(2) (on the a-axis), and from the apical O(4) atom are of about the same size. Only the O(3) atom (on the b-axis) contributes noticeably less than the others (see middle part of Fig.3). The contribution to the DOS from the O(4) atom at this energy is also important as we show in the lower part of the figure.

At VHs$_2$ (-54 meV), the total DOS has a small kink as we can see in Fig. 1. This is the nearest to the Fermi energy VHs which is filled with occupied states, as we have stated before. At VHs$_2$ the overwhelming contribution per atom comes from the chains as it is clear from Fig. 3. Notice that the contribution from atoms in the plane is of the same order of magnitude than the one from O(4). If the VHs are of importance in HTSC, it might be important to include this other contributions as well. We recall again the simultaneous simulation of tunneling, specific heat and ultrasonic attenuation experiments including the planes, the chains and the c-axis as active scenarios. In that formulation the chains were assumed to become superconducting by proximity effect. In spite of the fact that the BCS formulation of the proximity effect does not support the idea that the chains could become superconducting, the idea of including more scenarios is worth more analysis.

A. Contribution per atom

At $E_F$, each atomic contribution from Cu(1), Cu(2), O(2) and O(3) are and of about the same order. The O(1) and O(4) atoms contribute about half the previous one and Y has a very small almost negligible contribution. We did not take into account Ba atoms. In the next Table I, we summarize these results.
Table I - Contribution to the Density of States from states associated to different atoms in YBa$_2$Cu$_3$O$_7$. We show rounded percentages. The contribution is per atom not per unit cell. Notice the important one from the chain atoms to VHs$_2$. They do not sum up to 100%. For that we have to take into account that there are several repeated atoms in the unit cell (two Cu(2), for example, see Table II). Y has a minor contribution in all cases (not shown) and we did not take into account the Ba atoms contribution which is negligible at this energies.

| Atom  | VHs$_1$ | VHs$_2$ | E$_F$ | VHs$_3$ |
|-------|---------|---------|-------|---------|
| Cu(1) | 11      | 32      | 10    | 9       |
| Cu(2) | 11      | 6       | 12    | 11      |
| O(1)  | 10      | 30      | 5     | 4       |
| O(2)  | 13      | 6       | 12    | 14      |
| O(3)  | 4       | 5       | 13    | 14      |
| O(4)  | 11      | 2       | 5     | 4       |

B. The total contribution in the unit cell.

The contributions per atom are interesting in showing that atoms located out of the plane do contribute to the DOS about the same than the in-plane ones. The real difference seems to be therefore mainly in the number of planes in a unit cell. We compare here the respective contributions from the planes, the b-chains and the O(4) apical atom, per unit cell.

In Table II, we compare the contribution of the plane states, i.e., the states coming from the O(3), Cu(2), and O(2) atoms, counted twice, the b-axis chain states, Cu(1)-O(1), (counted once) and the apical O(4) (counted twice). These are 10 of the 13 atoms constituting the unit cell. The contribution of states coming from Y and from the two Ba atoms are negligible at these energies. We stress that Table II compares the percentage contribution per unit cell.

| Subgroup  | VHs$_1$ | VHs$_2$ | E$_F$ | VHs$_3$ |
|-----------|---------|---------|-------|---------|
| Planes    | 55      | 32      | 74    | 78      |
| Chain     | 21      | 62      | 15    | 13      |
| O(4)$_1$  | 23      | 5       | 10    | 8       |

Table II - The contribution percentages (rounded) from the planes, the chains and the O(4) states to the Density of States (DOS) per unit cell (not per atom). Here the sum should be 100% if all the atoms were included.

From this table, we can conclude that the contribution per unit cell of the planes is very important. Therefore, a 2D description of HTSC takes into account the most important quantitative contributions. This is in agreement with the relative success of the Van Hove scenario formulation. But from the same table, we see that the contribution to the DOS from the chains is not only important but also that the nearest-to-E$_F$ occupied Van Hove singularity is populated by states coming mainly from the chains. These states should take part in the formation of the condensate when in the superconducting state and it will not
be surprising that in YBa$_2$Cu$_3$O$_7$ at least part of the condensate lies in the chains as Dow and Blackstead have postulated for superconducting PrBa$_2$Cu$_3$O$_7$\cite{Dow2000}. By not including the chains one may lose certain effects as the simulation of their own experiments by Cucolo et al.\cite{Cucolo2001} seems to prove. The conclusion is that the chains cannot be neglected in a proper description of YBa$_2$Cu$_3$O$_7$.

**IV. CONCLUSIONS**

We have reproduced the band structure calculations by DeWeert et al.\cite{DeWeert2002} and have analyzed in detail the energy landscape in the First Brillouin Zone for energies around the Fermi level. We have found three Van Hove Singularities nearby. Two below and one above at energies $-230$, $-54$ and $+27$ meV, respectively. We have label them VHS$_1$, VHS$_2$ and VHS$_3$. They are located at $\mathbf{k}_1=(0.42\frac{\pi}{a}, 0.13\frac{\pi}{b}, 0)$, $\mathbf{k}_2=(0, \frac{\pi}{b}, 0)$ and $\mathbf{k}_3=(0, \frac{\pi}{2b}, 0)$ where the notation is conventional.

In an energy interval of about 100 meV around $E_F$, the contribution per atom of the Cu(1), Cu(2), O(1), O(2), O(3) and O(4) are roughly equal. See Fig. 3 and Table I. When we take them per unit cell, the planes appear to contribute in a very important way. This fact shows that from the quantitative point of view a 2D formulation makes sense. This is in agreement with the relative success of the Van Hove scenario. But the contribution of the out-of-plane atoms is very relevant and qualitative effect are lost when they are not included. The simulation by Cucolo et al.\cite{Cucolo2001} of their own experiments seems to illustrate this point. In VHS$_2$, the nearest-to-$E_F$ occupied Van Hove singularity, we find the contribution from the chains more important than the one coming from the planes. Also the contribution from the apical O(4) is not at all negligible within an interval of energy around $E_F$ of the order of 10 times the gap. At $-200$ meV, we find a maximum in the $E$ vs. $\mathbf{k}$ space. At this energy, the contribution per atom from the O(4) apical atom is the most important.

Finally, we conclude, first, that if the Van Hove singularities are relevant to superconductivity in the YBa$_2$Cu$_3$O$_7$, the chains have to be included. In a more general way, we conclude, from the composition of the Density of States around $E_F$, that though a 2D description of YBa$_2$Cu$_3$O$_7$ takes into account most of the weight in the DOS around the Fermi level, it might be insufficient to account for superconductivity. A 3D scenario seems compulsory to account for the details. In particular, it would not be surprising that part of the condensate lies in the chains also in YBaCuO as it was argued to be for PrBaCuO very recently.

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FIGURES

FIG. 1. The total density of states (DOS) in the vicinity of the Fermi energy, $E_F$. We found three Van Hove singularities. One at -230 meV, another at -54 meV and one just above $E_F$, at +27 meV. The origin is at $E_F$.

FIG. 2. We have located the Van Hove singularities studying directly the 3D ($k_z = 0$) energy landscape and finding the saddle points that produce them. Here we merely show two paths in the FBZ perpendicular to each other. We see that in one direction $E(k)$ has a minimum and in the other it has a maximum. In 3D a saddle point emerges. The upper part (a) is devoted to VHs$_1$, the middle part (b) to VHs$_2$ and the lower part (c) to VHs$_3$.

FIG. 3. In this set of figures we show the composition of the density of states (DOS) in an interval of 800 meV around the Fermi level. We find important contributions at the energies where a Van Hove singularity lies, from states that do not come from the CuO$_2$ planes although these contribute the most at $E_F$ to the DOS. See text for more details.
Wave vector

Energy (eV)
Density of states (states/eV)

Energy (eV)