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How T_c can go above 100 K in the YBCO family

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Abstract. We report the results of the electronic structure calculation of a newly discovered member of the YBCO high-T_c family, i.e., $Y_3Ba_5Cu_8O_{18}$ (Y358) with $T_c > 100$, based on the full-potential linearized augmented plane waves method (FP-LAPW) of density functional theory in the generalized gradient approximation (GGA). The evolution of the number of hole carriers in different sites of the CuO_2 planes and CuO chains has been investigated in comparison with the other YBCO family members, i.e., Y123, Pr123, Y124, and Y247. The results suggest that pumping hole carriers out of the chains toward the planes enhances the transition temperature. The band structure calculations have been performed for Y358, and the results show similar features with the other family members. Most notably, a van Hove singularity forms near the X point of the Brillouin zone below the Fermi level and within the energy of the buckling phonon mode, for which the interplay is discussed.

PACS. 71.15.Mb Density functional theory, local density approximation, gradient and other corrections – 71.20.-b Electron density of states and band structure of crystalline solids – 74.72.-h Cuprate superconductors (high-T_c and insulating parent compounds)

1 Introduction

$YBa_2Cu_3O_7$ (Y123) is the first superconductor discovered with the transition temperature above the liquid nitrogen boiling temperature [1]. This compound has been an interesting subject for much research and yet scientists are hopeful to find better superconducting compounds with similar composition. There is no real change in the superconductivity of Y123 when the Y atom is substituted by other trivalent rare earths elements except for Pr, by which superconductivity suppresses [2]. $YBa_2Cu_4O_{16}$ (Y124) and $Y_2Ba_4Cu_7O_{15}$ (Y247) are other two familiar members of the YBCO-family, but with lower transition temperatures: 84 K [3] and 65 K [4], respectively. Like the other high-T_c cuprate superconductors, the most important element of this family is the CuO_2 planes, in which the electrons pair.

In the YBCO family, like in the other cuprates, the T_c and the Cu-O-Cu bond buckling angle of the CuO_2 plane are correlated, and both go through a maximum with doping, but in the YBCO family the optimum buckling angle is larger than in the other cuprates [5]. This is also an implication of the important role of the out-of-plane buckling phonon mode of the oxygen atoms in the cuprates. The other distinctive structural elements of this family are formation of the CuO chains and double-chains (two neighboring chains displaced parallel to each other by half lattice parameter). In this family the chains are believed to play the role of the carrier reservoirs with minor contribution to the conductivity of the system; and doping of the carriers occurs by pumping oxygen into the chains. Y123 has two CuO_2 planes and one chain, where two planes are symmetrically equivalent. Y124 has one inequivalent plane and one double-chain, and Y247 has two inequivalent planes, one chain, and one double-chain.

The enhancement of T_c under applying pressure on Y123 [6] suggests that we may yet improve T_c at ambient pressure in the YBCO family by either chemical substitutions or structural deformations. A new member of the YBCO family has been reported with transition temperature above 100 K [7]. We have synthesized and characterized a few samples of a new YBCO compound by the solid-state reaction method with T_c about 102–116 K (different T_c values are for different synthesis conditions) [8]. The chemical formula of this compound is $Y_3Ba_5Cu_8O_{18}$ (Y358) with the crystal structure as depicted in Figure 1. This compound is synthesized with similar simple procedure but cheaper than Y123, and is potentially a better choice for the industrial and large scale applications. Y358 has five CuO_2 planes and three single chains which are respectively labeled as planes I to V and chains I to III in Figure 1; one of the planes, i.e., the plane III, has no apical

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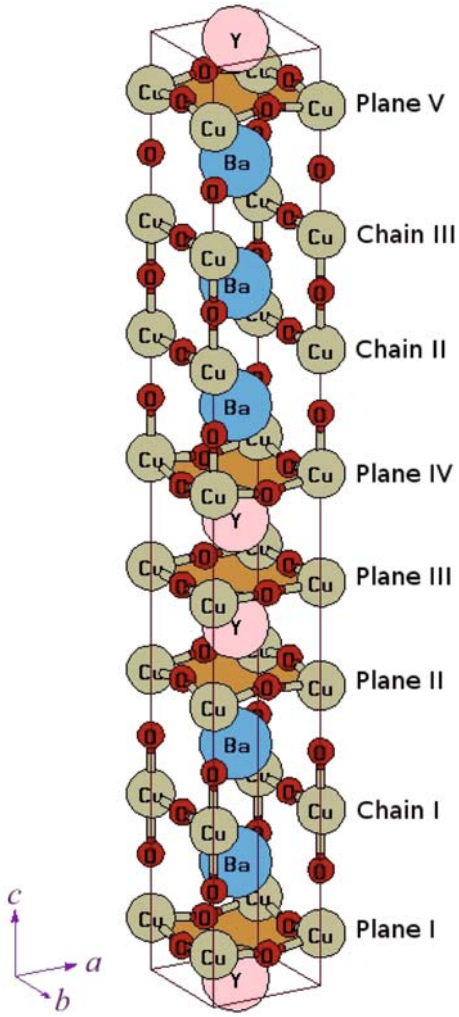

Fig. 1. (Color online) Crystal structure of Y358 with five CuO_2 planes I to V and three CuO chains I to III.

oxygen atoms. It has been claimed that the maximum T_c in each cuprate family belongs to the member with three CuO_2 planes [9], but the reason is not clear. In Y358 in fact, we have two groups of successive CuO_2 planes which are separated by the insulating layers, a two-plane group and a three-plane group. So, the situation is somehow different from the original cuprates where all the CuO_2 layers are in succession. Different proposals can be examined for this new compound which has higher T_c with five copper oxide planes.

The electron-phonon interaction and strong electron correlations are two main candidates for the origin of the mechanism of high-T_c superconductivity phenomenon. Hole concentration in the copper oxide planes plays an important role in every theory of superconductivity, so, studying the evolution of the carriers in different sites of the high-T_c superconductors versus doping or structural deformations, etc. may help to better justification of any mechanism candidate for HTSC. Of course, the well known dome-shaped T_c versus doping – and many other parameters – is almost always applicable for cuprates, but the problem is that in some compounds one really has no knowledge of the actual relation between the amount of chemical doping with the actual doped carriers in the planes or other sites of that compound. This is the case for the YBCO family in which it is not clear how the number of carriers in the planes and the chains change with the oxygen content.

In this paper, we will consider the answer to the above question for different YBCO family members, i.e., compare the doped hole carriers in different sites of the planes and chains in all member compounds. We will also present the results of a density functional theory (DFT) study on the hole concentration in the planes and the chains of different members of the YBCO family. Also, we will present for the first time the results of the band structure calculations of the Y358 compound and investigate the coupling of a near Fermi level van Hove singularity (VHS) with the buckling phonon mode of the oxygen atoms in Y358. This, we hope would stimulate the search for higher superconducting transition temperatures in the Y-based cuprates as well as in the other HTSCs.

2 Computational details

All the calculations are performed utilizing the WIEN code which is a powerful full potential DFT code [10]. The employed basis set is the linearized augmented plane waves to which the local orbitals can be added (LAPW+lo). However, though using DFT is not very suitable when studying the strongly correlated materials like the high-T_c cuprate superconductors, but this is the only available ab-initio approach which could efficiently be used when we aim to study the differences between some similar structures and their effects on the superconducting state. Applicability of the DFT approach to the cuprate superconductivity was settled after the experimental data showed good agreement with the computational results. For example, the experimental structural parameters and Fermi surfaces [11], and also the calculated phonon modes [12,13] are in very good agreement with the experiment. Anyway, DFT can be used as a starting point before one performs a strongly correlated calculation, as most of the initial parameters of the strongly correlated models such as Hubbard U, hopping integrals, carrier concentration, etc. can be obtained within DFT.

The structural parameters of Y123, Y124, and Y247 have been set from the experiment [14–16], and for Y358 we have used the data from the X-ray diffraction analysis of our own samples [8]. For Pr123 we have used the parameters of Y123 for better comparison. The muffin tin radii have been set equal to 2.35, 2.35, 2.5, 1.75, and 1.55 for the Y, Pr, Ba, Cu, and O atoms, respectively. These values were kept unchanged in all calculations which enabled us to compare the charge inside every muffin tin sphere relative to similar atomic spheres in other compounds. The GGA has been used for the exchange and correlation functional. The energy separation between the core and valence states has been set equal to 6.0 Ry. The APW+lo basis set has been selected for the d orbitals of

the Cu atoms and for the f orbitals of the Pr atom to have a more effective convergence. For all other atomic orbitals, we have used the LAPW basis set. The RK_{max}, L_{max}, and G_{max} parameters have been set equal to 7.0, 10, and 14, respectively. In addition to the energy convergence, the charges have also been converged. The number of k points sampled in the first Brillion zone has been set equal to 500, 500, 300, 200, and 200 for Y123, Pr123, Y124, Y247, and Y358, respectively.

3 Results and discussion

3.1 Carriers in the planes and the chains

The theoretical models for superconductivity often use the hole concentration in the CuO_2 planes as their input parameter. In some high-T_c superconductors like $La_{1-x}(Sr \text{ or } Ba)_xCu_2O_4$ this quantity has a direct relation with doping. But, usually, determination of the actual amount of the hole content is not easy or straightforward. An important case is the 66 K plateau in the T_c versus doping diagram of Y123. The reason for this plateau is not obvious, but it is usually being ascribed to that the hole concentration remains constant in the planes when the oxygen content changes from 6.6 to 6.8, due to rearrangement of the oxygen atoms in the basal planes (chains) [17]. The Cu-O bonding in cuprates has both the ionic and covalent nature, whence, one can study the changes in the hole content of the Cu and O sites by evaluating the partial charges inside the corresponding muffin tin spheres. This value is not the absolute amount of holes in a particular atomic site, neither is the absolute change in the number of carriers added to or removed from a site. But it shows the trend as how much the number of carriers rises or falls in an atomic site by changing an exterior parameter, which can be as important as the number of holes itself. As mentioned before, the muffin tin radii have been kept constant in all of the calculations to enable the comparison of the partial charges in different cases with each other. The Y123 system was kept as the reference system, and the atomic partial charges of other systems have been compared to this system to extract the probable changes.

Table 1 contains the calculated values of the changes in the number of holes in the Cu and O sites of the CuO_2 planes for different YBCO family compounds relative to that of Y123. In the CuO_2 plane of Pr123 and Y124, and in the plane III of Y358 the total number of holes are less than the number of holes in the planes of Y123, and in all other cases the total number of holes in the planes are more than in Y123. However, the T_c of Y358 is higher than that of Y123, but as it is known, the T_c of Y247 and Y124 are lower than Y123, and in Pr123 superconductivity is completely suppressed. Based on these data, it is concluded that the number of holes in the CuO_2 planes is not the only affecting parameter (we will come to the other affecting parameters when discussing the charges in the chains in the following paragraphs); and that the planes of Y123 are not optimally doped. The results show that the decrement of the number of holes suppresses superconductivity but its increment does not necessarily lead to higher T_c.

Table 1. Calculated hole content change in different sites of the CuO_2 planes of Y124, Y247, Y358, and Pr123 relative to that of Y123.

Compound		Cu	O(2)	O(3)	Total
Y124		–0.006	–0.004	–0.001	–0.011
Y247	Plane 1	0.006	–0.001	–0.001	0.004
	Plane 2	0.018	0.017	0.020	0.055
Y358	Plane I	0.000	0.022	0.021	0.043
	Plane II	0.001	0.023	0.030	0.054
	Plane III	–0.077	0.003	0.000	–0.074
	Plane IV	–0.009	0.024	0.022	0.037
	Plane V	0.030	0.047	0.046	0.123
Pr123		–0.037	–0.001	–0.001	–0.039

Table 2. Calculated hole content change in different sites of the CuO chains of Y247, Y358, and Pr123 relative to the chains (double-chain) of Y123 (Y124).

Compound		Cu	O	Total
Y247	Chain	0.049	0.036	0.085
	D-Chain	0.013	0.000	0.013
Y358	Chain I	–0.019	–0.038	–0.057
	Chain II	–0.010	–0.027	–0.038
	Chain III	–0.019	–0.031	–0.050
Pr123		–0.010	–0.003	–0.013

In Y124, the hole content at all the sites of the CuO_2 plane, i.e., Cu, O(2), and O(3) is lower than that of Y123. In Y247 the hole content of the oxygen sites are slightly decreased in the first plane, but the increment of the number of holes at the Cu site recovers this decrement. So, in total, an increase in the number of holes occurs. In the other non-equivalent plane of Y247, the hole content at all the sites increases.

In Y358, except for the Cu sites of the planes III and IV in which the hole content is decreased, in all other sites of the planes the hole carrier content is increased. In the plane IV the increment of the number of holes of the oxygen site quite recovers this decrement, and in total, this plane is better doped. But, in the plane III the increment of the carriers in the oxygen sites are marginal and this plane is very poor in the number of holes. This was expected since this plane lacks the apical oxygen which has important charge transferring role in doping of the neighboring planes [18]. Comparing this with the changes in the hole content of the Pr123 planes, it can be concluded that the decrement of the holes in the plane III of Y358 is so much as its possible superconductivity could be suppressed, or at least it has a marginal effect on superconductivity of the whole system. In the other hand, the change of the carrier number in the plane V may be enough to place this plane in the overdoped regime.

In order to find the other probable affective parameter(s), we have also calculated the charges in the chains and double-chains, which are seen in the Y124 and Y247 systems. Table 2 contains the change in the number of holes in the Cu and O sites of different CuO single and

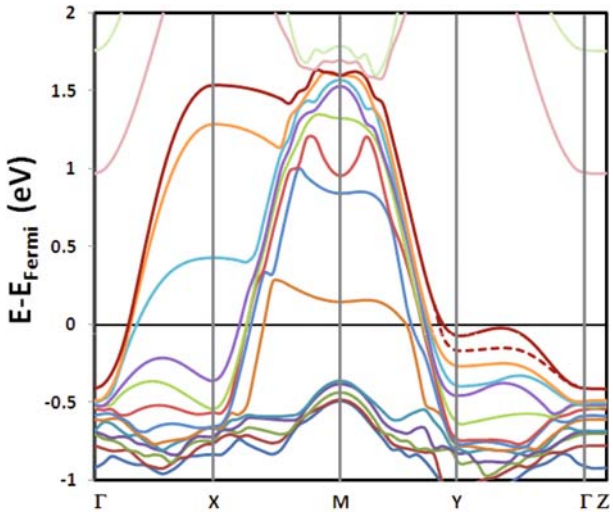

Fig. 2. (Color online) Band structure of Y358 in the energy interval of –1 eV to 2 eV relative to the Fermi energy (for the oxygen atom in the maximum buckling angle). The dashed curve shows the deformation of the band which constitutes a VHS below the Fermi level when the buckling angle is minimum.

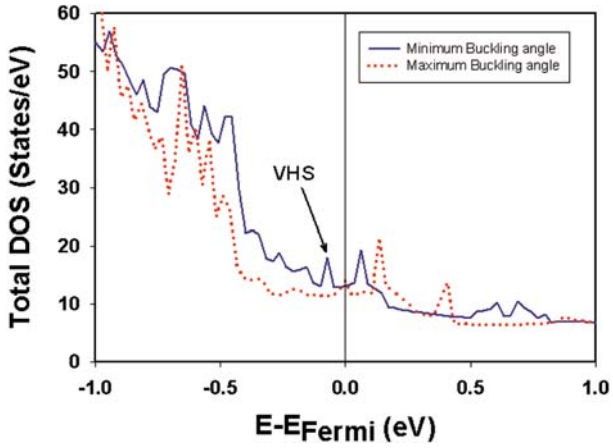

Fig. 3. (Color online) DOS of Y358 in the energy interval of –1 eV to 1 eV relative to the Fermi energy in the two extremes of oxygen atom displacements of the buckling phonon mode. The solid (dashes) line belongs to the minimum (maximum) buckling angles. The VHS is indicated on the figure.

double chains of different compounds of the YBCO family relative to that of Y123 and Y124, respectively. Comparing the amounts of carriers that a chain (in Y123) or double-chain (in Y124) can hold, indicates that each of the Cu-O strings of a double-chain contains fewer amounts of hole carrier. In Y247 the number of holes both in the chain and in the double-chain is greater than the number of holes in the chain of Y123 and the double-chain of Y124, respectively; and the hole increase in the chain is higher than in the double-chain. In contrast to the Y247 system with its rich doped chain and double-chain, in Y358 the chains have fewer holes with respect to Y123, and this is the only difference between the Y247 and Y358 systems in terms of the hole concentration of the planes and chains.

Collecting the results of all the calculations together, two conclusions could be made: 1) doping the planes of Y123 system with additional holes may enhance T_c; 2) decrement of the number of holes in the chains favors the T_c, perhaps by helping the planes to have a more 2D characteristic. In other words, one should pump more holes from the chains into the planes in order to obtain a higher-T_c superconductor in the YBCO family.

3.2 Band structure

The band structure and corresponding DOS of Y358 compound have been calculated and are depicted in Figures 2 and 3. Like the other members of the YBCO family [19,20], there are bands crossing the Fermi level which belong to the planes and chains. Here, eight bands cross the Fermi level with energy dispersions equal to 0.071, 0.123, 0.125, 0.131, 0.140, 0.145, 0.151, and 0.146 Ry.

Another feature of the Y358 band structure is the appearance of a VHS within –65 meV of the Fermi level in the (0, π) direction of the Brillouin zone. The "VHS scenario" has been an issue in the mechanism of cuprates [21]. Despite the undisputed presence of VHS in the cuprates, the VHS scenario has gone in and out of favor over the years [22,23]. The presence of a VHS at or near the Fermi surface can strongly influence the many-body interactions. It can enhance the electron-electron or electron-phonon interactions or cause anisotropic electron phonon coupling.

The obtained VHS in Y358 is much below the Fermi level in comparison with the other YBCO family members (–6 meV and –19 meV within the Fermi level in the Y123 and Y124 systems, respectively [22,24]) to play a direct role in the superconductivity. The VHSs more than a few meVs from the Fermi level cannot directly lead to superconductivity, but when they appear within a phonon energy of the Fermi level they remain as an important part of the theory. We have examined the behavior of VHS in Y358 with the displacement of the in-plane oxygen atoms according to the out-of-plane buckling phonon. This phonon mode has a similar energy value (∼50 meV) [13], and more importantly, it can couple to the anti-nodal electrons due to its small momentum transfer, just where the VHS appears. When the bucking angle is small, the VHS forms at energies far from the Fermi level (about –65 meV). By increasing the buckling angle, this VHS becomes closer to the Fermi level but also weaker, and eventually vanishes for large buckling angles. However, again, the topology (curvature) of the band, which determines the shape of the Fermi surface changes in the energies about –50 meV for large buckling angles, but the DOS does not diverge. This behavior can be ascribed to the changing of the Cu-O hopping integrals which becomes smaller (smaller band dispersions) when the buckling angle increases. These features all show a strong interplay between this phonon mode and the VHS in the Y358 system, which can enhance the electron-phonon interaction and lead to the anisotropic electron-phonon interaction. No matter what the origin of high-T_c is, the role

of VHSs and electron-phonon interaction cannot be overlooked. The differences between various compounds and their structures may be explained through these singularities and interactions.

4 Conclusions

We have presented here the electronic structure calculations of the newly discovered Y358 compound with $T_c > 100$ K. The hole content of different sites of its planes and chains has been compared to the other members of the YBCO family. Our results show that in the Y358 system the hole content in four of its five planes increases, and in the other plane which has no apical oxygen the hole content decreases. It is notable that in one of those four planes, the total amount of hole increase puts the plane in the overdoping regime. By comparing the charge differences in the chains, our results imply that in order to have a better superconductor with higher T_c in the YBCO-family, one should pump more holes from the chains to the planes.

The band structure calculations show similar features with the other YBCO compounds but with a VHS rather far from the Fermi level, which is sensitive to the out-of-plane buckling mode of the oxygen atoms. The discovery of Y358 compound is very promising in finding still better Y-based compounds with higher transition temperature. More investigations are needed experimentally and computationally to better understand how T_c correlates with different structures and with different arrangement of the building blocks of the YBCO family compounds.

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