Electronic Structure And The van Hove Singularity
Scenario In High-T_c HgBa\textsubscript{2}CuO\textsubscript{4+\delta} Superconductors

by
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The electronic structure and the hole concentrations in the high T_c superconductor HgBa\textsubscript{2}CuO\textsubscript{4+\delta} (\delta = 0, 1) has been investigated by employing a first principles full potential self-consistent LMTO method with the local density functional theory. The scalar relativistic effects have been considered. The hole concentrations of the Cu-d and O-p(x,y) orbitals are seen to be larger for the HgBaCuO\textsubscript{5} system than those of the HgBaCuO\textsubscript{4} solid. However, the van Hove singularity (vHs) induced Cu-d and O-p peak which is seen to lie comparatively away and above the Fermi level in the \delta=1 system shifts towards the Fermi level in the \delta=0 system. Thus, the superconducting behaviour appears to originate from the occurrence of the vHs peak at the Fermi level. The Fermi surface nesting area in the \delta=0 compound is seen to be larger than in the \delta = 1 compound. The calculation reveals that the increase in pressure on the crystal enhances the hole concentrations but without showing any optimum value.

On the other hand, the vHs peak approaches towards the Fermi level with pressure and crosses the Fermi surface near V/V_0 \approx 0.625 (V and V_0 are the crystal volumes at high and normal pressures, respectively). Our calculated value of the bulk modulus equal to 0.626 Mbar predicts the occurrence of this crossover at about 24 GPa which is in complete agreement with the experimental value. At this pressure the compound has maximum nesting area and self-doped behaviour.
I. INTRODUCTION:

The compound HgBa2CuO(4+δ) (δ = 0, 1) has been seen [1] to be superconducting with Tc=94°K. Schilling et al [2] have observed a Tc=133°K in a material containing HgBa2Ca2Cu3O30(8+δ) and HgBa2CaCu2O(6+δ). Quite recently, values of Tc as high as 164°K at high pressure have been reported in HgBa2Ca2Cu3O30(8+δ) samples [3,4].

In understanding the cause of the occurrence of superconductivity in high Tc superconductors, one cannot ignore the crucial role played by the CuO2 planes. In two-dimensions, one come across with the saddle points at symmetric points of the Brillouin zone which lead to logarithmic vHs in the electron density of states obtained even after assuming only nearest-neighbour hopping. It has been seen [5] that a simple reformulation of BCS theory in the weak coupling limit considering the occurrence of a vHs near the Fermi energy may lead to quantitatively different results. The value of Tc may be much higher achieving its maximum value when the van Hove singularity coincides with the Fermi energy.

In the present communication, we investigate the occurrence of the van Hove singularity in the Hg-based single CuO2 layer compounds HgBa2CuO(4+δ) (δ=0,1). Novikov and Freeman [6] and Rodriguez et al [7] have also performed a LMTO calculation for the δ=0 compound but have not investigated the pressure effects. Our similar results for HgBa2CaCu2O(6+δ) (δ=0,1) have been reported elsewhere [8]. The present LMTO method goes beyond the usually employed LMTO method in the atomic sphere approximation which has several limitations. The method is seen to predict the electronic structure, lattice constants, elastic constants, and phonon frequencies, for the simple systems III-V and II-VI semiconducting compounds like AlAs, CdTe, GaSb, ZnSe, ZnTe, ZnS etc [9]. Also, the parent compound CaCuO2 of the recently discovered high Tc oxide superconductors has been successfully studied [10].

II. CALCULATION AND RESULTS

The crystal structures of HgBa2CuO(4+δ) (δ=0,1) possess the space group P4/mmm. The lattice parameters of the tetragonal cell are the experimentally measured values i.e., a=3.8797 Å and c=9.509 Å. In HgBa2CuO5, the atomic positions in the unit cell are Cu:(0,0,0); O(1):(0.5a,0,0); O(2):(0,0.5a,0); and Ba:(0.5a,0.5a±0.294c);
$O(3):(0,0,\pm 0.294c)$; $\text{Hg}:(0,0,0.5c)$ and $O(4):(0.5a,0.5a,0.5c)$. For $\text{HgBa}_2\text{CuO}_4$, the atom $O(4)$ of the HgO plane has been removed.

The basis functions with $l \leq 4$ and of energies $-0.01$, $-1.0$ and $-2.3$ Ry were chosen for making the expansions of the products of the LMTO envelopes. The decays of these functions were taken as $\lambda^2 = -1$ and $-3$ Ry. Each atomic sphere has thus 50 functions. The local density potential of Hedin and Lundquist [ii] has been utilized. A spd basis each for the two high energies $-1.0$ and $-0.01$ Ry and a sp basis for the energy $-2.3$ Ry were employed for every real atom. It leads to a number $22$ of LMTO's per atom.

The muffin-tin (MT) spheres chosen to fill the space were slightly non-overlapping. The radii of these atomic spheres in atomic units were $\text{Cu}(2.0)$, $O(1.655)$, $\text{Ba}(3.35)$ and $\text{Hg}(2.05)$.

The valence states considered for the various atoms are $\text{Cu}(3d,4s,4p)$; $O(2s,2p,3d)$; $\text{Ba}(6s,6p,5d)$ and $\text{Hg}(6s,6p,6d)$. The core electrons are treated not in a frozen-core approximation but are allowed to relax. A number of 72 $k$-points obtained by the sampling method in the irreducible part of the Brillouin zone were employed in all the calculations. The $\delta=0$ compound shows minimum in the crystal energy at a volume ratio $(V/V_0)=1.05$, where $V_0$ is the experimental crystal volume for the $\delta=0.1$ sample. Novikov and Freeman [6] and Rodriguez et al [7] have reported results for a different set of valence states.

(i) Electronic Structure:

The dispersion curves for a number of symmetry points lying in the two different $k(x,y)$ planes have been depicted in Fig.1. They are $\Gamma = (0,0,0)$; $X = (\pi/a)(1,0,0)$; $M = (\pi/a)(1,1,0)$; $Z = (\pi/a)(0,0,a/c)$; $R = \pi(1/a,0,1/c)$ and $A = \pi(1/a,1/a,1/c)$. The origin of the energy is taken at Fermi level ($E_F$).

The electronic structure is very much two-dimensional. The dispersion of the valence bands along the $c$-axis i.e., along the symmetry direction $\Gamma-Z$ is quite small. The band structure in the two different planes along $k_x$ are very much similar.

In Figs. 1b, 1c and 1d, we have also depicted those parts of the dispersion curves for which the probability of any wave function on an atom
is equal or more than 0.2.

The single antibonding Cu-3d(x^2-y^2):O-2p(x, y) band crosses the Fermi surface in most of the shown symmetry directions in the k_z=0 plane [see Fig. 1(b)] and goes above E_F up to more than 2 eV.

The band structure for the HgBa2Cu05 is quite similar to that of HgBa2Cu04 except that in the former there is an overall shift of the valence bands towards the high energy side by 0.4 and the conduction bands by a large magnitude of about 3.5 eV.

The Hg-6p conduction states do not cross the Fermi surface making the compound not self-doped. Also no atom of the BaO and Hg planes contributes and are thus electronically inactive. In the δ=0 sample, the location of the saddle point of the crossover Cu-3d(x^2-y^2):O-2p(x, y) band changes with k_z; it varies from a

value -0.51 eV at X point to -0.37 eV (k_z=0.204) at R point. On the other hand, in the δ=1 sample, they appear at 0.40 eV at X and 0.18 eV at R points, respectively.
(ii) Density of States:

The computed local electron density of states for the $\delta=0$ compound is presented in Fig. 2. In the 6.0 eV wide valence band region, the main contributions arise from the Cu(3d) and the O(2p) states of the various oxygens lying in the layers of Cu-02 and BaO. The density of states at the Fermi level in the $\delta=1$ compound is very high equal to 7.24 states/eV as compared to 0.49 states/eV in the $\delta=0$ sample.

The most remarkable feature is shifting of the vHs peak originating from (Fig. 3) the Cu-3d($x^2-y^2$):O-2p(xy) states. In the $\delta=0$ compound it changes from -0.44 eV at X point to -0.37 eV at the R point which may drive the $\delta=0$ compound approaching to-wards the superconducting behaviour. On the other hand, in the $\delta=1$ compound these peaks appear above the Fermi level at 0.42 eV at X and 0.18 eV at R respectively. The appearance of the vHs peak above the Fermi level may result in the observed non-superconducting behaviour of the compound HgBa$_2$CuO$_4$. 

![Projected DOS at various atoms of the HgBa$_2$CuO$_4$ system.](image)
The other peaks like one appearing at about 0.33 eV in between the energy range 0.18 to 0.42 eV originate from the flatness of the bands in the different parts of the Brillouin zone.

(iii) Fermi Surface

The cross sections of the Fermi surface for the \( \delta = 0 \) and 1 compounds, in the two different \((k_x-k_y)\) planes i.e. \( k_z=0 \) and \( k_z=0.204 \) are shown in Fig. 4. We find nesting along the [100] and [010] directions. The shapes of the Fermi surface are circular for \( \delta = 1 \) but are rounded squares in \( \delta = 0 \) compound. The nesting area in both the \( k_z \)-plane in the \( \delta = 0 \) compound is greater than in the \( \delta = 1 \) compound. The change in the nesting area with the change of the location of the \( k_x-k_y \) plane along the \( k_z \)-axis is quite small in \( \delta = 0 \) compound, a behaviour different from that seen for the \( \delta = 1 \) compound. The three-dimensional surface will look like a tube.

<table>
<thead>
<tr>
<th>System</th>
<th>Atom</th>
<th>Orbitals</th>
<th>Hole Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgBa\textsubscript{2}CuO\textsubscript{4}</td>
<td>Cu d</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu p</td>
<td>0.108</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(Cu)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(Hg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgBa\textsubscript{2}CuO\textsubscript{5}</td>
<td>Cu d</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu p</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(Cu)</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(Ba)</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(Hg)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(iv) Hole Concentrations:

The hole concentrations at the various atomic sites are shown in Table I. The main contributions arise from the Cu(3d) and the O(2p) states. Every oxygen atom of the unit cell contributes towards the hole density. The individual contributions of the Cu(3d) and O(2p) states are comparable.

(v) Charge Density:

The charge densities around the various atoms for the $\delta = 0$, 1 compounds are very much similar except the missing charge around O(4) atom in the $\delta = 0$ compound. The charge density for the $\delta = 1$ compound for the vertical plane (110) passing through the Cu-atom shown in Fig.5 reveals that there is little charge between the Cu atom and the oxygen atom lying in the Ba-O layer (03) because of the large separation between these atoms. Also, the binding between O3 and Hg is quite strong because of the presence of high charge density between them. The oxygen atom O4 lying in the Hg-plane is weakly bound both to the Hg and Ba atoms and is likely to be knocked out of its parent site easily.

FIG.4 Cross-sections of the Fermi surface in the extended Brillouin zone scheme in two planes, $k_z=0$ (dashed curve) and $k_z=0.204$ (continuous curve) for (a) HgBa2CuO4 and (b) HgBa2CuO5.
(vi) Effect Of Pressure:

The variation of the crystal energy with the lattice volume gives a bulk modulus equal to 0.626 Mbar. The variation of the hole concentrations with pressure are depicted in Table 2. We do not find any optimum value although the hole concentration at both Cu and O atoms increase with pressure. The increase in pressure on the crystal shifts the vHs peak towards the Fermi level (see Fig. 6.) and near \( V/V_0 = 0.625 \), the vHs peak is pinned at Fermi level. This volume corresponds to a pressure of about 24 GPa which is in perfect agreement with the experimental observation of Chu et al [3]. It is noted that that Hg \( 6(p) \) conduction states at the optimal volume crosses the Fermi level and makes it now self-doped, a behaviour seen [8] in the Hg based oxide superconductors containing two or more CuO\(_2\) layers. Further, the Fermi level touches the Brillouin zone boundary making the Fermi surface

![Charge Density of HgBa\(_2\)CuO\(_4\) in (1,-1,0) plane](image)

**FIG. 5** Distribution of the electron charge density in the (1,-1,0) plane containing Cu and O atoms of HgBa\(_2\)CuO\(_4\). The contours are drawn for an interval of 0.015 e/(a.u.)\(^3\) up to maximum value of 0.14 e/(a.u.)\(^3\).

![HgBa\(_2\)CuO\(_4\)](image)

**FIG 6** Deviation of vHs peak from Fermi level with pressure.
Table 2: Variation of Hole Concentrations with Crystal Volume for HgBa\(_2\)CuO\(_4\).

<table>
<thead>
<tr>
<th>(\frac{v}{v_0})</th>
<th>Hole Concentration</th>
<th>Electrons</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td>0.90</td>
<td>0.22 0.28</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>0.12 0.14</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.10 0.12</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>0.10 0.12</td>
<td>0.22</td>
<td></td>
</tr>
</tbody>
</table>

HgBa\(_2\)CuO\(_4\)

Fermi Surface

FIG. 7 Cross sections of the Fermi surface for cry-

nesting area maximum. There appear small
electron pockets due
to Hg 6p states at
point R as shown in
Fig. 7.

V. CONCLUSIONS

The present results predict the occurrence of the
vHs peaks above and
below the Fermi
level in the \(\delta=1\) and
\(\delta=0\)
compounds, respectively. This
is in agreement with the observation of the superconducting
behaviour in the oxygenated
HgBa\(_2\)CuO\(_4+\delta\) \((\delta=0.1)\)
compound. The
nesting of the Fermi
surface in the \(\delta=0\)
compound is of a higher degree than
in the \(\delta=1\) compound.
The
hole concentrations of the Cu-d\((x^2-y^2)\) and
the O-p(x,y)
orbitals in the \(\delta=0\)
compound increase
with pressure on the
crystal. The deviation of the vHs peak from the Fermi level also decreases with the pressure on the crystal and the vHs is pinned at Fermi level at a pressure of about 24 GPa in perfect agreement with experimental data. The nesting area of the Fermi surface is also maximum at this optimum value.

VI ACKNOWLEDGEMENTS

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REFERENCES