

ELECTRONIC STRUCTURE AND THE VAN HOVE SINGULARITY
SCENARIO IN HIGH- T_c $\text{HgBa}_2\text{CuO}_{4+\delta}$ SUPERCONDUCTORS

by

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The electronic structure and the hole concentrations in the high T_c superconductor $\text{HgBa}_2\text{CuO}_{4+\delta}$ ($\delta = 0, 1$) 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_5 system than those of the HgBaCuO_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 to-wards 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 $\text{HgBa}_2\text{CuO}(4+\delta)$ ($\delta = 0, 1$) has been seen [1] to be superconducting with $T_c=94^\circ\text{K}$. Schilling et al [2] have observed a $T_c=133^\circ\text{K}$ in a material containing $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}(8+\delta)$ and $\text{HgBa}_2\text{CaCu}_2\text{O}(6+\delta)$. Quite recently, values of T_c as high as 164°K at high pressure have been reported in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}(8+\delta)$ samples [3,4].

In understanding the cause of the occurrence of superconductivity in high T_c superconductors, one can not ignore the crucial role played by the CuO_2 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 T_c 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 CuO_2 layer compounds $\text{HgBa}_2\text{CuO}(4+\delta)$ ($\delta=0,1$). Novikov and Freeman [6] and Rodriguez et al [7] have also performed a LMTO calculation for the $\delta=0$ compound but have not investigated the pressure effects. Our similar results for $\text{HgBa}_2\text{CaCu}_2\text{O}(6+\delta)$ ($\delta=0,1$) 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 CaCuO_2 of the recently discovered high T_c oxide superconductors has been successfully studied [10].

II. CALCULATION AND RESULTS

The crystal structures of $\text{HgBa}_2\text{CuO}(4+\delta)$ ($\delta=0,1$) possess the space group $P4/mmm$. The lattice parameters of the tetragonal cell are the experimentally measured values i.e., $a=3.8797 \text{ \AA}$ and $c=9.509 \text{ \AA}$. In $\text{HgBa}_2\text{CuO}_5$, the atomic positions in the unit cell are $\text{Cu}:(0,0,0)$; $\text{O}(1):(0.5a,0,0)$; $\text{O}(2):(0,0.5a,0)$; $\text{Ba}:(0.5a,0.5a,\pm 0.294c)$;

O(3): (0,0,+0.294c); Hg: (0,0,0.5c) and
O(4): (.5a,.5a,.5c). For HgBa₂CuO₄, 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 [11]
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 Cu(2.0),
O(1.655), Ba(3.35) and Hg(2.05).

The valence states considered for the various
atoms are Cu(3d,4s,4p); O(2s,2p,3d); Ba(6s,6p,5d) and
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
 Γ -Z is quite small. The band structure in the two
different planes along k_z 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

HgBa₂CuO₄

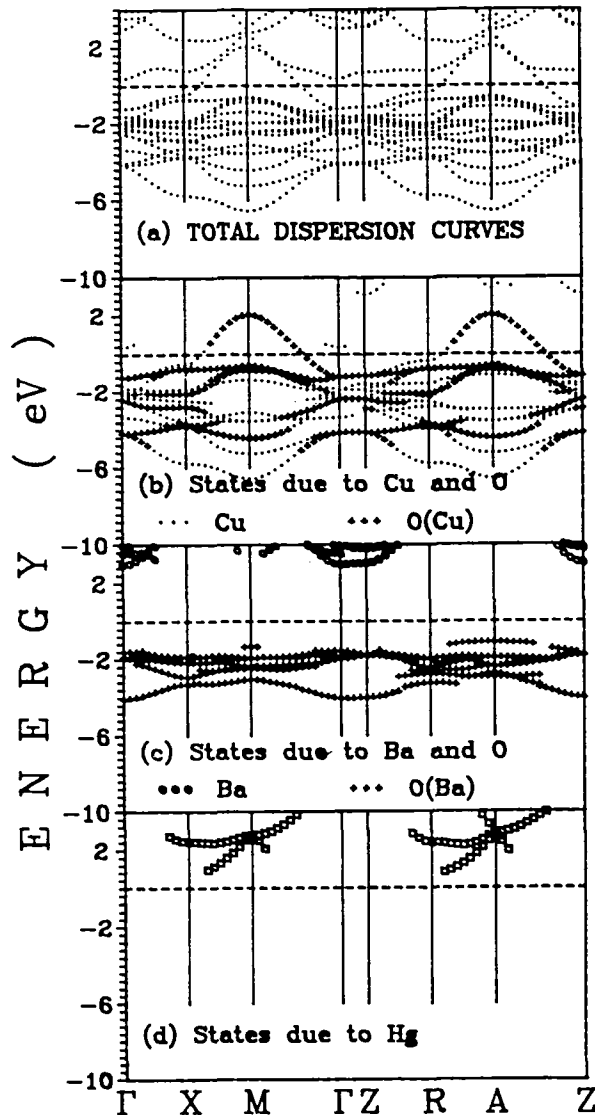


FIG.1 Electronic band structure for HgBa₂CuO₄ compound in two k_z - planes and also along k_z direction.

value -0.51 eV at X point to -0.37 eV ($k_z=0.204$) at R point. On the other hand, in the $\delta=1$ sample, they appear at 0.40 eV at X and 0.18 eV at R points, respectively.

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 upto more than 2 eV.

The band structure for the HgBa₂CuO₅ is quite similar to that of HgBa₂CuO₄ 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 $\delta=0$ 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

(ii) DENSITY OF STATES :

The computed local 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-O2 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.

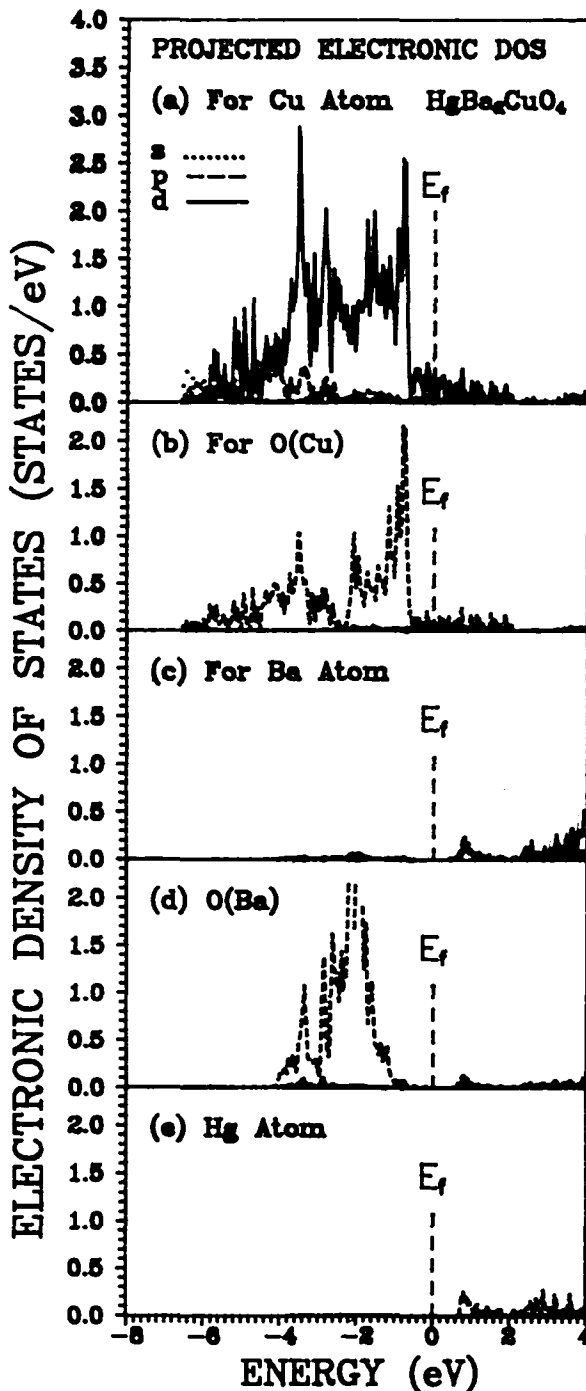


FIG.2 Projected DOS at various atoms of the HgBa₂CuO₄ system.

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 HgBa₂CuO₅.

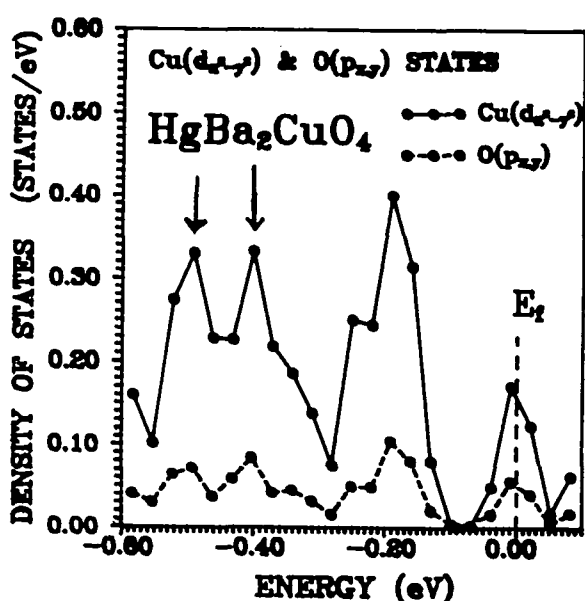


FIG.3 Cu-3d(x^2-y^2) & O-2p(x,y) density of states around the Fermi level of HgBa₂CuO₄ with an extended energy scale.

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 - planes 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.1: HOLE CONCENTRATIONS FOR HgBa₂CuO₄ AND HgBa₂CuO₅.

| System | Atom | Orbitals | Hole Concentration |
|------------------------------------|-------|----------|--------------------|
| HgBa ₂ CuO ₄ | Cu | d | 0.09 |
| | O(Cu) | p | 0.108 |
| HgBa ₂ CuO ₅ | Cu | d | 0.23 |
| | O(Cu) | p | 0.39 |
| | O(Ba) | p | 0.50 |
| | O(Hg) | p | 0.68 |

(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 atoms of the unit cell contributes to-wards the hole density. The individual contributions of the Cu(3d) and O(2p) states are comparable.

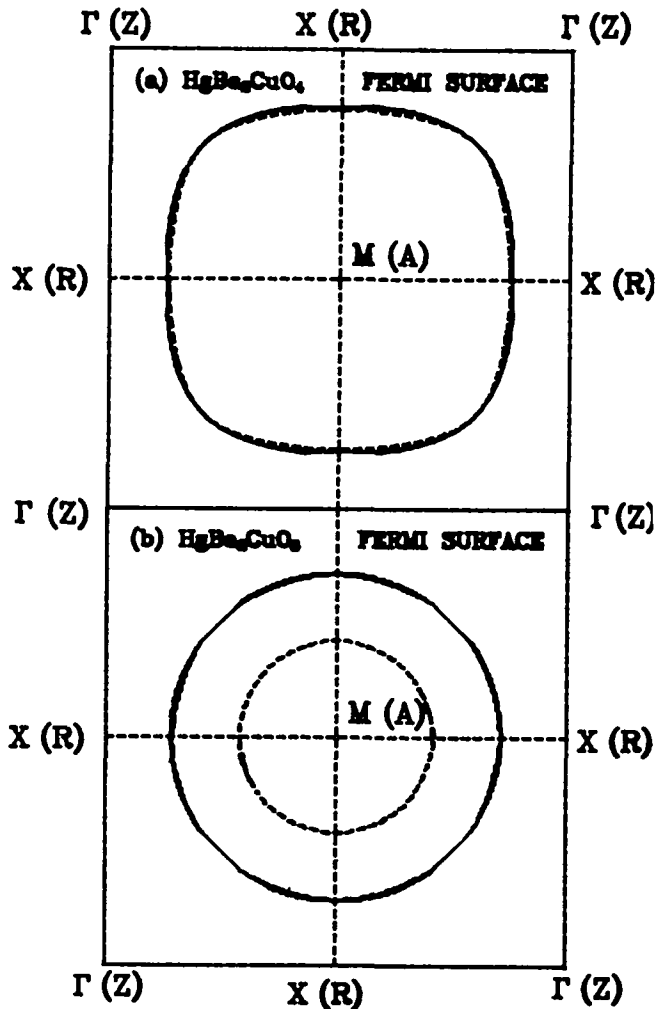


FIG.4 Cross-sections of the Fermi surface in the extended Brillouin zone scheme in two planes, $k_z=0$ (dashed curve) and $k_z=0.204$ (continuous curve) for (a) $\text{HgBa}_2\text{CuO}_4$ and (b) $\text{HgBa}_2\text{CuO}_5$.

(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 (O3) 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.

(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

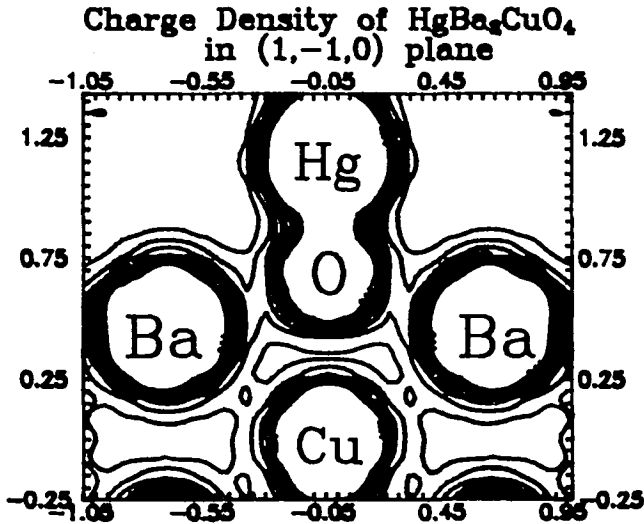


FIG.5 Distribution of the electron charge density in the (1,-1,0) plane containing Cu and O atoms of HgBa₂CuO₄. The contours are drawn for an interval of .015 e/(a.u.)³ up to maximum value of 0.14 e/(a.u.)³.

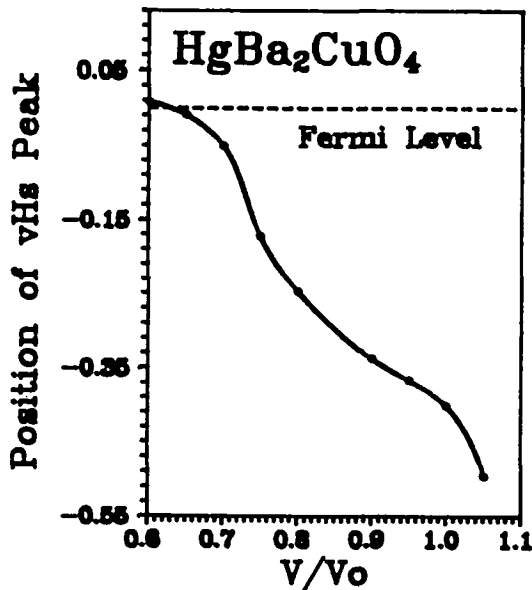


FIG 6 Deviation of vHs peak from Fermi level with pressure.

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 CuO₂ layers. Further, the Fermi level touches the Brillouin zone boundary making the Fermi surface

TABLE.2 : VARIATION OF HOLE CONCENTRATIONS WITH CRYSTAL VOLUME FOR $\text{HgBa}_2\text{CuO}_4$.

| v/v_0 | Hole Concentration | | |
|---------|--------------------|-------|-------|
| | Cu | O(Cu) | Total |
| 0.90 | 0.22 | 0.28 | 0.50 |
| 0.95 | 0.12 | 0.14 | 0.26 |
| 1.00 | 0.10 | 0.12 | 0.22 |
| 1.05 | 0.10 | 0.12 | 0.22 |

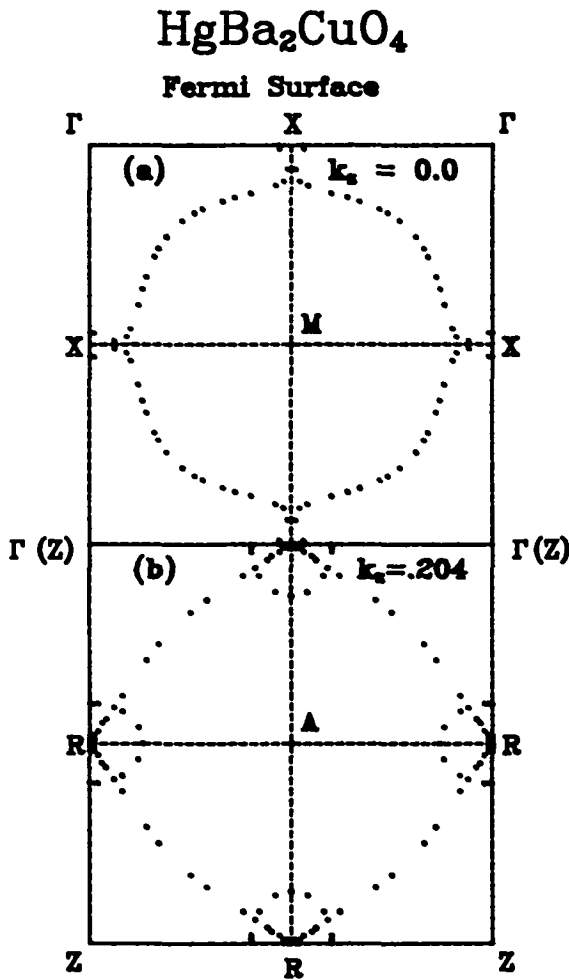


FIG.7 Cross sections of the Fermi surface for crystal volume $v/v_0=0.625$ for $\text{HgBa}_2\text{CuO}_4$.

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 $\text{HgBa}_2\text{CuO}_{4+\delta}$ ($\delta=0.1$) 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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