Structural, Dynamical & Electronic Properties of CaCuO₂

by

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The scalar relativistic version of an accurate first principles full potential self-consistent linearized muffin tin orbital (LMTO) method has been employed for describing the physical properties of the parent system of the high-Tc oxide superconductors, i.e., CaCuO₂. The presently employed modified version of the LMTO method is quite fast and goes beyond the usual LMTO ASA method in the sense that it permits a completely general shape of the potential and the charge density. Also, in contrast to LMTO ASA, the present method is also capable of treating distorted lattice structures accurately. The calculated values of the lattice parameters of pure CaCuO₂ lie within 3% of the experimentally measured values for the Sr-doped system Ca(.86)Sr(.14)CuO₂(2). The computed electronic structures and the density of states is quite similar to those of the other oxide superconductors, except of their three-dimensional character because of the presence of strong coupling between the closely spaced CuO₂ layers. The van Hove singularity peak appears slightly below the Fermi level and a small concentration of oxygenation /or/ substitutional doping may pin it at the Fermi level. The calculated frequencies for some symmetric frozen phonons for undoped CaCuO₂ are quite near to the measured data for the Sr-doped CaCuO₂.

I. INTRODUCTION

The present LMTO method is seen to produce the electronic structure, cohesive energy, lattice constants, elastic constants, phonon frequencies, mode Grüneisen and strain parameters for the simple systems like Si, C etc [1]. Very recently, the method has been successfully applied also for the III-V and II-VI semiconducting compounds like AlAs, CdTe, GaSb, ZnSe, ZnTe, ZnS etc [2,3]. The influence of structural relaxation of the atoms on the valence-band off-set at the lattice matched
interfaces of II-VI and III-V semiconductors ZnTe/GaSb(110) and the lattice mismatched interface ZnS/ZnSe(001) has been investigated [4]. Very recently the van Hove singularity scenario and hole concentrations at different pressures for the Hg-based oxide superconductors have been investigated [5].

A compound CaCuO2 is obtained if the number of CuO2 planes is allowed to increase indefinitely (n -> \infty). Thus, CaCuO2 is the infinite number of CuO2 layers limit of the above superconductors and is seen to be insulating [6]. Tc might increase with n. The n = \infty material appears to be more difficult to dope. However, more recently (CaSr)CuO2 has been doped successfully and an electron type superconductivity has been seen [7]. In practice, the n = \infty structure is not formed with only Ca ion on A site, a material with some Ca substitution by Sr, Ca(0.86)Sr(0.14)CuO(2) has been prepared. The Sr-mixed compound is seen to be narrow band semiconductor. For details of the LMTO method we refer to the earlier papers [1-4].

II. CALCULATION AND RESULTS

The CaCuO2 structure as shown in Fig.1 has a space group P4/mmm (D4h(i)). The atomic positions in the unit cell are Cu:(0,0,0); O(1):(.5a,0,0); O(2):(0,.5a,0); Ca:(.5a,.5a,.5c).

For the Sr-doped sample the experimental lattice parameters are a=3.86 A and c=3.2 A°. The bond lengths are Cu-O(1) = Cu-O(2) = 1.93 A° and Ca-O(1) = Ca-O(2) = 2.50 A°.

In the present calculation, the basis employed for making expansions of the products of the LMTO envelopes included functions with l \leq 4 and of energies -0.01, -1.0 and -2.3 Rydberg and with decays given by \lambda=-1 and -3 Rydberg. The set will include 50 functions.
for each atomic sphere. The local density potential
of Hedin and Lundquist has been employed. An absolute
convergence to better than 1.5 mRy/atom is obtained
with spd basis of 22 LMTO's/atom for each atom
including O. The number of atoms in unit cell were
taken to be four.

The muffin tin (MT) spheres were chosen to be
slightly smaller than touching and the radii for Cu,
O and Ca were taken as 1.88, 1.64 and 2.99 atomic
units(a.u.), respectively. The states Cu(3d,4s,4p),
O(2s,2p) and Ca(3p,3d,4s) are taken as the valence
band electrons. An empty sphere has been included at
(0,0,.5c) in the calculation.

Variations both in the lattice parameter 'a'
and the ratio c/a were investigated. The results
are shown in Figs. 2 & 3, respectively. One finds
energy minimum for a volume of the unit cell
V = 0.925 V₀ and c/a = 1.00, where V₀ is the
unit cell volume for a = 3.86 Å (in fact, these
lattice parameters correspond to the
experimental values for the Sr doped
CaCuO₂). So the values of a and c are
quite close to those for Sr- doped
material. The
calculated value of 'c' is within 3% of the experimental value. The calculated value of bulk modulus is 1.99 Mbar.

The charge transfer from the muffin tin spheres (i.e., the difference between the atomic number and charge lying within the MT sphere) of Cu, O and Ca are 1.65, 0.56, and 0.62 electron charges, respectively. The total electron charge per unit cell outside the MT spheres is 3.39e.

(A) ELECTRONIC STRUCTURE

The calculated band structure along some symmetry directions is presented in Fig. 4. The various symmetry points of the Brillouin zone in units of 2\pi/a are \Gamma(0,0,0); X(.5,0,0); M(.5,.5,.6); Z(0,0,.6); R(.5,0,.6) and A(.5,.5,.6). As the spacing between the two successive CuO2 layers is smaller than the intraplaner Cu-O separation within the CuO2, the bands along the c-direction show appreciable dispersion although smaller than the dispersion seen within the x-y plane (or Cu-O2 layer). The Fermi level is set at origin of energy.

![CaCuO2 Dispersion Curves](image)

**FIG. 4** Dispersion curves for the CaCuO2 system.

The lowest 11 bands lying in the energy interval range of about 9 eV near and below Fermi level arise mainly from the Cu(3d) and O(2p) states. This spread (~ 9 eV) of energy bands is similar to that calculated by Mattheiss and Hamann [8] and by Singh et al [9] using LAPW method and by Korotin an Aniscimov [10] using the LMTO-ASA method. The uppermost band crossing the Fermi level corresponds to the anti-bonding Cu-d(\textit{x}^2-\textit{y}^2):O-p(x,y) states. The lower parts of the Ca(3d) bands lying above Fermi level overlap the antibonding
near $\Gamma$ and $A$ symmetric points.

In order to see the nature of the dispersion in another plane shifted in the c-direction, we have also included in Fig. 4 the dispersion curves in the $2\pi/a[0,0,0.6]$ direction. There appear saddle points at -0.81 eV at X point and at -0.19 eV at R point.

In the calculation of the total density of states (DOS), a sampling method for 196 k points in the irreducible part of the Brillouin zone with a Gaussian energy broadening of 0.002 Ry was employed. The calculated DOS for the self-consistent calculation is shown in Fig. 5. The DOS shows the main features which are quite similar to those of the other oxide high-Tc cuprates. The projected densities at various atoms have also been shown in Fig. 6. At Fermi level, the main contributions arise from Cu(3d) and O(2p) states.
The high degree of the nesting of the Fermi surface is likely to give rise to singularities in the generalized k-dependent electronic susceptibility of the two-dimensional system and may result in the electronically-driven instabilities such as the incommensurate charge or spin density waves.

B. PHONON FREQUENCIES

The variation of the internal energy of the solid with the various types of static deformations in the small displacement limit has been employed for calculating the frozen phonon frequencies at the \( \Gamma (k=0) \) point of the Brillouin zone. In CaCuO\(_2\) in all, there are six optical modes out of which five are infrared active and the remaining sixth mode comprising of the out of (CuO\(_2\)) plane vibrations of oxygen atoms in opposite direction is silent. The frequencies of these vibrations along with their eigenvectors are presented in Table I. The frequencies have been calculated by determining the harmonic force constant after fitting the energies of the distorted structure for several amplitudes with a polynomial containing terms up to third degree. In order to see the reliability of the estimates of these calculated values we have also included in the table the measured values for the Sr-doped CaCuO\(_2\). The frequencies for undoped sample are quite close to the observed values for the Sr-doped sample except for Eu mode which involves the motion of all the atoms.

FIG. 8 Valence charge density contours in the \((0,-1,1)\) plane in an interval of 0.015 e/(a.u.)\(^3\) up to a maximum value of 0.12 e/(a.u.)\(^3\).
FIG. 9 Cross-sections of the Fermi surface in the extended Brillouin zone scheme in two planes (a) $k_x = 0.0$ and (b) $k_x = 0.603$ for CaCuO$_2$.

III. CONCLUSIONS:

The LMTO method which is comparatively simple and faster than the LAPW method is able to predict one electron energy spectrum of CaCuO$_2$ quite well. Values for the bulk modulus and the frozen phonon frequencies have been obtained. The phonon frequencies for the undoped CaCuO$_2$ are quite near to those measured for the Sr-doped sample.
TABLE I. Frequencies of the various phonon modes for CaCuO$_2$ in cm$^{-1}$

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Mode Symmetry</th>
<th>Displaced Atoms</th>
<th>Components of atomic displacements</th>
<th>Calculated freq. for CaCuO$_2$</th>
<th>Exptl. freq. for Sr-doped CaCuO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Au</td>
<td>Cu, Ca</td>
<td>$Z_1 - Z_2$</td>
<td>213</td>
<td>186</td>
</tr>
<tr>
<td>2.</td>
<td>Au</td>
<td>O</td>
<td>$Z_3 - Z_4$</td>
<td>316</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Au</td>
<td>Cu, O, Ca</td>
<td>$\begin{pmatrix} Z_1 - Z_2 \ -Z_3 \ -Z_4 \end{pmatrix}$</td>
<td>422</td>
<td>421 (440)</td>
</tr>
<tr>
<td>4.</td>
<td>Eu</td>
<td>Cu, Ca</td>
<td>$\begin{pmatrix} X_1 - Y_1 \ -X_2 + Y_2 \end{pmatrix}$</td>
<td>323</td>
<td>230 (240)</td>
</tr>
<tr>
<td>5.</td>
<td>Eu</td>
<td>Cu, O, Ca</td>
<td>$\begin{pmatrix} -X_1 - Y_1 \ -X_2 - Y_2 \ +Y_3 - X_4 \end{pmatrix}$</td>
<td>306 (40)</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Eu</td>
<td>Cu, O</td>
<td>$\begin{pmatrix} -X_1 - Y_1 \ +X_3 - Y_4 \end{pmatrix}$</td>
<td>634</td>
<td>597 (663)</td>
</tr>
</tbody>
</table>

The displacements of the various atoms are denoted by Cu($X_1,Y_1,Z_1$), Ca($X_2,Y_2,Z_2$), O$_1$(X$_3,Y_3,Z_3$) and O$_2$(X$_4,Y_4,Z_4$).

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REFERENCES


