Electronic structure of perovskite related La$_2$CuSnO$_6$

D.L. Novikov $^{a,1}$, A.J. Freeman $^{a,*}$, K.R. Poeppelmeier $^b$, V.P. Zhukov $^c$

$^a$ Science and Technology Center for Superconductivity, Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208-3112, USA

$^b$ Science and Technology Center for Superconductivity, Department of Chemistry, Northwestern University, Evanston, IL 60208-3112, USA

$^c$ Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, GSP-145, Ekaterinburg, Russian Federation

Received 9 May 1995

Abstract

The band structure of La$_2$CuSnO$_6$ in both its real and idealized crystal structure was determined using the local density full-potential linearized muffin-tin orbital (LMTO) method. Unlike the case for all other high-$T_c$ copper-based materials, the Fermi energy for the undoped crystal is located exactly on the van Hove saddle-point singularity, which may be the main reason for the lattice distortions observed in the real material. We suggest that a possible way, if any, to drive this compound into the superconducting state is to be achieved via electron doping. For several reasons, we do not expect a high $T_c$ value.

A series of papers have appeared on the synthesis of new compounds containing structural units of Al, Ga, Sn along with the CuO$_2$ planes that are common for high-$T_c$ superconductors. These compounds are La$_2$CuSnO$_6$ [1], LaSrCuAlO$_5$ [2], LaSrCuGaO$_5$ [3], and RESr$_2$GaCu$_2$O$_7$ [4-6], RE$_2$Sr$_2$MCu$_2$O$_9$ (M = Al, Co, Ga) [7].

The crystal structure of the first compound, La$_2$CuSnO$_6$, is closely related to the structure of the high-$T_c$ copper-based superconductors (e.g. Hg-1201, TI-2201), but contains layers of CuO$_2$ and SnO$_6$ octahedra connected by oxygen atoms. However, according to magnetic-susceptibility measurements [8], the doped compound appears not to be superconducting down to at least 5 K. The nature of the conductivity of this compound is not understood nor, in particular, why all attempts to drive it into the metallic state have failed. For this reason, we turn to the possible understanding that can be obtained from electronic structure calculations. In this paper, we report on results obtained from an electronic structure investigation of La$_2$CuSnO$_6$ using the first-principles full-potential linear muffin-tin orbital method (FLMTO).

The crystal structure of La$_2$CuSnO$_6$ includes four formula units per unit cell (Fig. 1(a)). The main structural feature that makes the crystal structure complex is the buckling of the CuO$_2$ planes. Owing to this buckling, there are deviations in the geometry of the crystal from the orthorhombic structure: oxygen octahedra around the Cu and Sn cations are strongly tilted and the La cations are displaced to-
ward the Cu–O layer. The distortions give rise to two copper, two tin, and four lanthanum sites in the unit cell [1].

We have performed calculations for both the real (buckled) structure and the ideal one which makes it possible to reduce the size of the unit cell to one formula unit and hence to simplify the band-structure analysis. The ideal structure was deduced by flattening the Cu–O planes (i.e., removing the buckling) and removing the tilting of SnO$_6$ octahedra, while preserving the length of the most covalent Cu–O bonds (Fig. 1(b)). The unit-cell parameters and atomic positions for this structure are presented in Table 1.

The calculations were performed using the FLMTO method [9] in a spin-restricted scalar-relativ-
Table 1
Atomic coordinates (in units of the lattice constant) and MT-sphere radii for idealized LaSrCuSnO$_6$ used in the FLMTO calculations ($a = 7.385$ a.u., \(c/a = 2.178\))

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(R_{MT}) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.0</td>
<td>0.0</td>
<td>1.09</td>
<td>1.845</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.99</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.5</td>
<td>0.0</td>
<td>1.09</td>
<td>1.845</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.501</td>
<td>1.845</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>1.845</td>
</tr>
<tr>
<td>La</td>
<td>0.5</td>
<td>0.5</td>
<td>0.643</td>
<td>3.10</td>
</tr>
</tbody>
</table>

A large number of calculations has revealed some common features in the electronic band structures of the high-\(T_c\) superconductors. The most important seems to be the presence of a strongly hybridized Cu 3d–O 2p derived band crossing the Fermi energy \(E_F\). Also favorable to the onset of the superconductivity is the presence of a van Hove saddle-point singularity \(\nu\)HS in the closest vicinity of the Fermi level. Hence, these are the main points that we will consider in our discussion.

The FLMTO band structure of the idealized La$_2$CuSnO$_6$, which makes this compound very different from other high-\(T_c\) materials, is that the Fermi level is located exactly at the \(\nu\)HS even for the undoped case. The \(\nu\)HS in this structure appears to be strongly dispersed along X–A in the BZ, which is clearly seen from Fig. 3; the overall dispersion of the \(\nu\)HS is about 0.5 eV. From the DOS (cf., Fig. 4) it is seen that \(E_F\) is located on the broad peak, consisting mainly of Cu 3d, O(2) and O(3) 2p states. This again shows the difference of this compound from the usual band composition of high-\(T_c\) Cu–O based materials, where the main contribution to the DOS at \(E_F\) comes from Cu 3d and “in-plane” oxygen (O(1) in our case) 2p states.

Let us now consider the real La$_2$CuSnO$_6$ structure with four formula units per unit cell. Fig. 5 shows the band structure of this compound along the same symmetry lines in the BZ as for the ideal structure. The total and l-projected DOS's are presented in Fig. 6. The main changes in the electronic structure in the vicinity of \(E_F\) are:

1. the \(\nu\)HS related peak in the total DOS splits into two peaks; this reduces the high density of states at that cross \(E_F\) around M and A in the BZ. A remarkable feature of the band structure of ideal La$_2$CuSnO$_6$, which makes this compound very different from other high-\(T_c\) materials, is that the Fermi level is located exactly at the \(\nu\)HS even for the undoped case. The \(\nu\)HS in this structure appears to be strongly dispersed along X–A in the BZ, which is clearly seen from Fig. 3; the overall dispersion of the \(\nu\)HS is about 0.5 eV. From the DOS (cf., Fig. 4) it is seen that \(E_F\) is located on the broad peak, consisting mainly of Cu 3d, O(2) and O(3) 2p states. This again shows the difference of this compound from the usual band composition of high-\(T_c\) Cu–O based materials, where the main contribution to the DOS at \(E_F\) comes from Cu 3d and “in-plane” oxygen (O(1) in our case) 2p states.

The FLMTO band structure of the idealized La$_2$CuSnO$_6$, along some symmetry lines in the simple tetragonal BZ is presented in Fig. 2, where X = (\(\pi/a\); 0; 0), M = (\(\pi/a\); \(\pi/a\); 0), R = (\(\pi/a\); 0; \(\pi/c\)) and A = (\(\pi/a\); \(\pi/a\); \(\pi/c\)). As is typical for all Cu–O based high-\(T_c\) superconductors the quasi-two-dimensional Cu–O derived free-electron-like d\(\pi\)\(\sigma\) band crosses \(E_F\). There are also some additional bands, mainly arising from the O(2) 2p (apical oxygen) and O(3) 2p (oxygen in SnO$_2$ planes) states,
Fig. 3. FLMTO band structure in the Fermi energy region of idealized LaSrCuSnO₆ along Γ−X−R−Z directions.

Fig. 5. FLMTO band structure of the real LaSrCuSnO₆ in the Fermi energy region.

Fig. 4. Total and projected DOS for the idealized LaSrCuSnO₆.

Fig. 6. Total and projected DOS for the real LaSrCuSnO₆.
$E_F$ from 2.4 states/eV per Cu atom for the ideal structure to 0.8 states/eV per Cu atom for the real one; and

(2) the band character in the vicinity of $E_F$ gets back to what is regarded to be a common high-$T_c$ composition (i.e., Cu 3d–O(1) 2p states with only a small admixture of the apical O(2) and O(3) 2p states). It needs to be stressed that $E_F$ is again located exactly in the middle of the vHS, which is now effectively split by the lattice distortions (buckling of Cu–O planes and tilting of the SnO$_6$ octahedra).

In view of these results, we can discuss the possibility of achieving superconducting properties for this material. The first, and probably most important difference between the electronic structure of La$_2$CuSnO$_6$ and its idealized counterpart from all “conventional” high-$T_c$ materials is the location of $E_F$ exactly in the energy region of the vHS for the undoped case. This high DOS makes the system unstable, and this is the most likely reason for the crystal distortions observed in the real structure that effectively reduce the value of the total DOS at $E_F$ and make the distorted compound more stable. If one recalls the empirical “recipe” for achieving superconductivity, one must first consider driving the initially semiconducting material into a metallic state. This is usually possible by appropriate electron or hole doping. A second step is the “optimization” of the doping, which usually should lead to moving $E_F$ into close vicinity with the vHS. As is seen from the band structures of both the idealized and real structures, both steps cannot be realized simultaneously. Any kind of doping will immediately move $E_F$ away from the vHS and, moreover, for the real structure this doping will lead to the moving of $E_F$ onto DOS peaks of the split vHS, which apparently may make the structure unstable and hence energetically unfavorable. This may be one of the reasons for the failure of attempts [8] to drive the system into a metallic state. Thus, the Mott–Hubbard picture of the electronic structure of this material proposed in Ref. [8] should be regarded as an appropriate one.

If one manages to make the ideal crystal of La$_2$CuSnO$_6$ (with flat Cu–O planes) by means of high pressure, or suitable chemical additions, one may try to dope this compound with electrons in order to achieve the superconducting onset. And we believe, the electron doping is the only possible way to achieve this goal, since this is the only way to get rid of the O(2), O(3) 2p states and to bring the composition of the states at $E_F$ to be of the Cu 3d–O(1) 2p (in-plane) type, and also to make the states at $E_F$ more two-dimensional-like as in all “conventional” high-$T_c$ copper-based superconductors. But if successful, we cannot expect a high value of $T_c$, because doping moves $E_F$ away from the vHS, which would be unfavorable for reaching high $T_c$ values.

Clearly, further investigations of this compound are very interesting from the fundamental point of view. If a superconducting state (even with a low $T_c$ value) can be obtained with this material by taking into account our considerations, it may further enhance the role of the van Hove singularity in achieving the optimum $T_c$ and the ability of LDA band-structure approaches to analyze and predict new and “optimal” high-$T_c$ materials.

In conclusion, we have performed LDA FLMTO band-structure analyses of La$_2$CuSnO$_6$ in its real and idealized crystal structures. In striking contrast to all high-$T_c$ copper-based compounds, we show that the Fermi energy for the undoped material is located exactly at the van Hove saddle-point singularity. This seems to be the main reason for the observed crystal structure distortions. Based on the band-structure analysis, we believe that La$_2$CuSnO$_6$ is not a good candidate for high-$T_c$ superconductivity. Nonetheless, we point out that one possible way to achieve a superconducting transition may be via electron doping accompanied by an attempt to flatten the Cu–O planes.

Acknowledgements

We thank M. Methfessel for an early version of his FLMTO code. This work was supported by the National Science Foundation (through the Northwestern University Science and Technology Center for Superconductivity, Grant No. DMR 91-20000, and by a grant of computer time at the Pittsburgh Supercomputing Center supported by its Division of Advanced Scientific Computing).
References