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Electronic structure of perovskite related La_2CuSnO_6

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Abstract

The band structure of La_2CuSnO_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_2CuSnO_6 [1], $LaSrCuAlO_5$ [2], $LaSrCuGaO_5$ [3], and $RESr_2GaCu_2O_7$ [4–6], $RE_2Sr_2MCu_2O_9$ (M = Al, Co, Ga) [7].

The crystal structure of the first compound, La_2CuSnO_6, is closely related to the structure of the high-T_c copper-based superconductors (e.g. Hg-1201, Tl-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_2CuSnO_6 using the first-principles full-potential linear muffin-tin orbital method (FLMTO).

The crystal structure of La_2CuSnO_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-

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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-

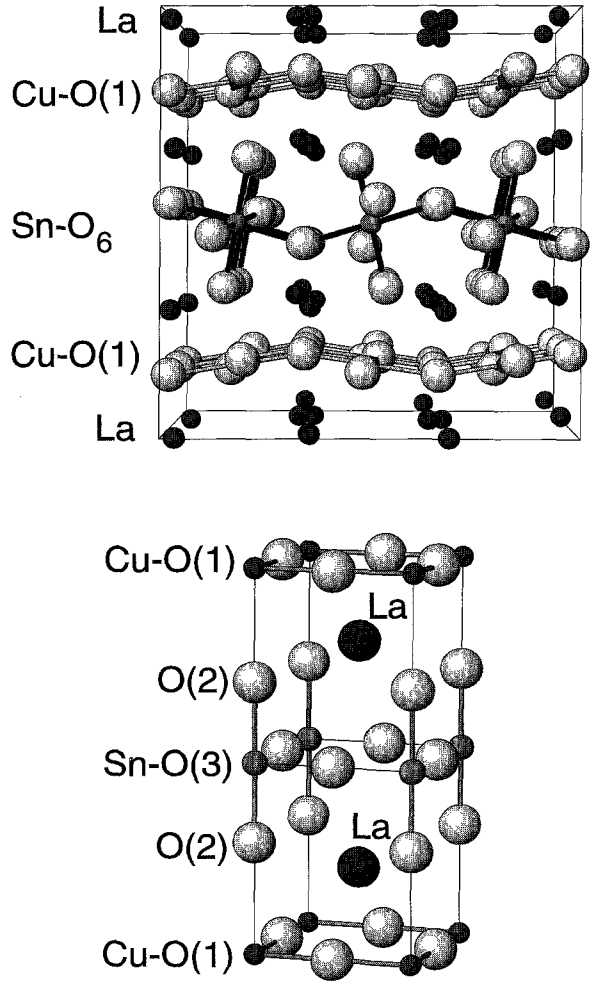

Fig. 1. Crystal structure of $LaSrCuSnO_6$; (a) real structure, (b) idealized one.

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., $c/a = 2.178$)

Atom	x	y	z	R_{MT} (a.u.)
Cu	0.0	0.0	1.09	1.845
Sn	0.0	0.0	0.0	1.99
O(1)	0.5	0.0	1.09	1.845
O(2)	0.0	0.0	0.501	1.845
O(3)	0.0	0.5	0.0	1.845
La	0.5	0.5	0.643	3.10

istic mode with atomic Cu $3d^{10}4s^1$, Sn $5s^25p^24d^{10}$, La $6s^25p^65d^1$, and O $2s^22p^4$ orbitals treated as valence band electrons and Cu $3s^23p^6$, Sn $4s^24p^6$ and La $5s^2$ treated as semicore states (in a second energy window). We used a triple-kappa basis set for each type of atom with angular momentum, l, up to 2 for Cu, Sn, O, and up to 3 for La for $\kappa^2 = -0.01$ Ry, and up to 1 for $\kappa^2 = -1.0$ and -2.3 Ry. The charge density was calculated exactly in the muffin-tin spheres (radii are listed in Table 1) for angular momentum components up to $l = 5$. The same l cut-off was used when interpolating in the interstitial region over Hankel functions with energies -1 and -3 Ry. The Brillouin zone (BZ) integrations were carried out using a 637 for the ideal structure and 132 k point mesh for the real one.

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 (vHS) 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_2CuSnO_6 along some symmetry lines in the simple tetragonal BZ is presented in Fig. 2, where X = (π/a; 0; 0), M = (π/a; π/a; 0), R = (π/a; 0; π/c) and A = (π/a; π/a; π/c). As is typical for all Cu–O based high-T_c superconductors the quasi-two-dimensional Cu–O derived free-electron-like dpσ 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, that cross E_F around M and A in the BZ. A remarkable feature of the band structure of ideal La_2CuSnO_6, which makes this compound very different from other high-T_c materials, is that the Fermi level is located exactly at the vHS even for the undoped case. The vHS 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 vHS 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_2CuSnO_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 vHS related peak in the total DOS splits into two peaks; this reduces the high density of states at

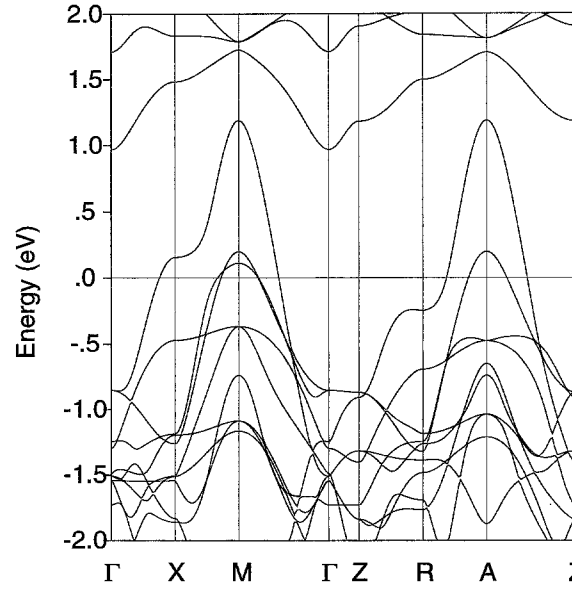

Fig. 2. FLMTO band structure in the Fermi energy region along some high symmetry directions of idealized $LaSrCuSnO_6$.

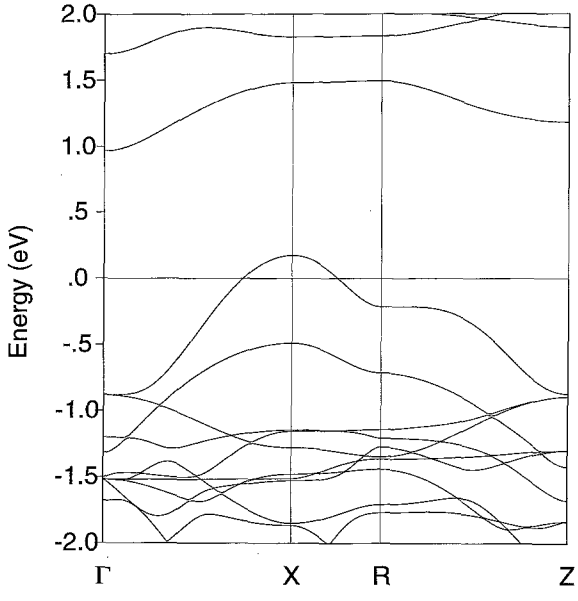

Fig. 3. FLMTO band structure in the Fermi energy region of idealized $LaSrCuSnO_6$ along Γ–X–R–Z directions.

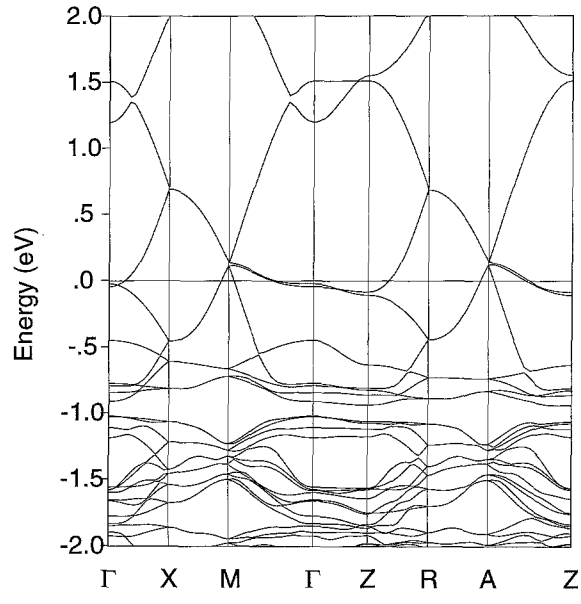

Fig. 5. FLMTO band structure of the real $LaSrCuSnO_6$ in the Fermi energy region.

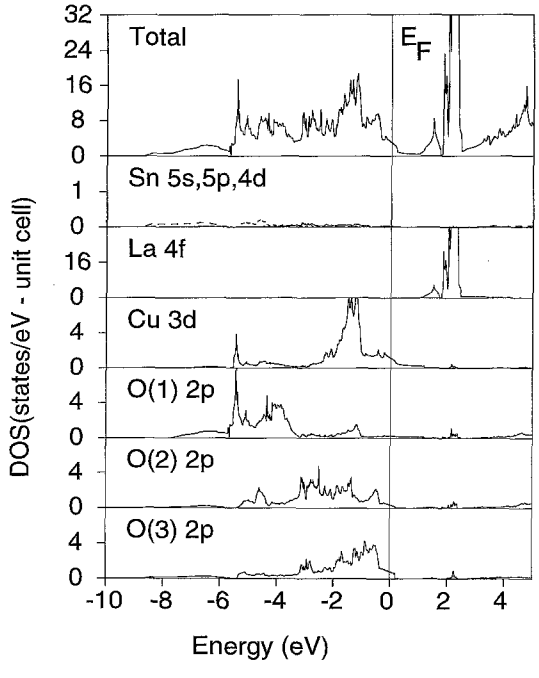

Fig. 4. Total and projected DOS for the idealized $LaSrCuSnO_6$.

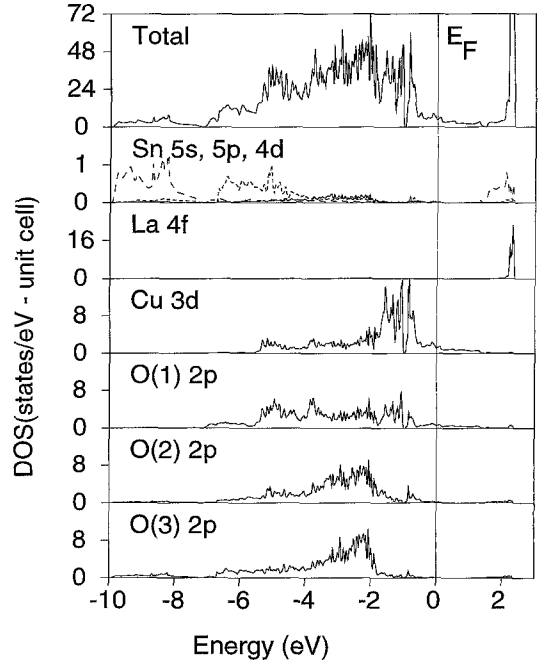

Fig. 6. Total and projected DOS for the real $LaSrCuSnO_6$.

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_2CuSnO_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_2CuSnO_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_2CuSnO_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_2CuSnO_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.

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