

DFT Calculation of Electronic Structure for the $\text{CaLaBaCu}_3\text{O}_7$ Superconducting Perovskite

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Resumen

Se reportan las propiedades estructurales y electrónicas de la perovskita $\text{CaLaBaCu}_3\text{O}_7$ en la fase cristalográfica tetragonal. Este material tiene un carácter superconductor con una temperatura crítica alrededor de 80 K. En el compuesto $\text{CaLaBaCu}_3\text{O}_7$, la transición tetragonal a ortorrómbico no aparece cuando se disminuye el contenido de oxígeno, como ocurre en el caso del $\text{YBa}_2\text{Cu}_3\text{O}_7$. A pesar de su importancia, son pocos los cálculos teóricos de la estructura electrónica y de bandas de energía para esta familia de perovskitas. Se presentan los posibles mecanismos superconductores en el plano de Cu-Cu-O_2 y cadenas O , en este tipo de material. Los cálculos se realizaron para el compuesto $\text{CaLaBaCu}_3\text{O}_7$ en el estado normal por medio del método FP-LAPW, en la aproximación GGA, siempre dentro del formalismo de la teoría del funcional de densidad (DFT). En primer lugar, el estudio consistió en encontrar la energía del compuesto, el volumen óptimo y el módulo de volumen. También se optimizó la relación c/a , donde a y c son los parámetros de red de la celda cristalográfica tetragonal. A partir de estos resultados, se llevó a cabo un estudio detallado de las propiedades electrónicas para este material. El objetivo de esta investigación es la determinación de las relaciones de dispersión y el cálculo de la densidad de los estados (DOS). También se determinó la proyección de la DOS en los orbitales atómicos. Se concluye que el orden de Cu y los átomos de oxígeno en los planos estructurales Cu-O_2 son importantes para el comportamiento superconductor del $\text{CaLaBaCu}_3\text{O}_7$.

Palabras clave: DFT, estructura electrónica, superconductor de alta temperatura, $\text{CaLaBaCu}_3\text{O}_7$.

Abstract

Structural and electronic properties of $\text{CaLaBaCu}_3\text{O}_7$ perovskite material in the characteristic tetragonal crystallographic phase are reported. This system has a superconductive character with a critical temperature around 80 K. In the $\text{CaLaBaCu}_3\text{O}_7$ compound, the tetragonal to orthorhombic transition does not appear when the oxygen content is diminished, as occurs in the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$. In spite of their importance, there are few theoretical calculations of electronic structure and energy bands for this perovskite family. This knowledge is important since we wished to know the possible superconducting mechanisms in the Cu-O_2

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plane and Cu-O chains. We performed calculations for the CaLaBaCu₃O₇ at the normal state by means of the FP-LAPW method, in the GGA approximation, within the formalism provided by the Density Functional Theory (DFT). First, the study consisted to find the energy of the compound, the optimal volume and the bulk modulus. Also the relation c/a was optimized, where a and c are the lattice parameters of the tetragonal crystallographic cell. From these results, we perform a detailed study of electronic properties for the perovskite compound. The aim of this study is the determination of dispersion relations and Densities of States (DOS) calculation. The projection of DOS on the atomic-like orbital was also determined. From our results it is conclude that ordering of Cu and O atoms in the Cu-O₂ structural planes is relevant for the occurrence of superconductivity in CaLaBaCu₃O₇ material.

Keywords: DFT, electronic structure, high temperature superconductor, CaLaBaCu₃O₇.

1. Introduction

Since the discovery of high temperature superconductivity by Bednorz and Müller [1], the study of pairing mechanisms in the cuprate oxide materials has been performed from several points of view. In order to analyze the electronic contribution to the density of states of each constituting elements of oxide material, in last years, calculations for the high temperature superconductor (HTS) YBa₂Cu₃O₇ in the orthorhombic structure have been made [2]. The cuprate CaLaBaCu₃O₇ belongs to the YBa₂Cu₃O₇'s family [3]. CaLaBaCu₃O₇ has a tetragonal crystalline structure, with lattice parameter $a = 7.256$ Bohr and $c = 22.349$ Bohr, and evidences a critical temperature $T_c \approx 80$ K. CaLaBaCu₃O₇ material is an YBa₂Cu₃O₇ prototype, where 40 % of Y sites are occupied by Ca ions and 60 % by La ions. In the same form, one of Ba sites is occupied by a distribution of Ca and La ions. This particular distribution makes that O(1) and O(5) ions, which are around Cu(1) ion, conform a tetragonal structure, independently of total oxygen contain in the system. However, as known in other superconducting perovskite oxides, the crystalline structure of CaLaBaCu₃O₇ is characterized by the presence of Cu-O₂ planes, which are considered as

responsible by the superconducting behavior in these materials. The objective of this work is to present a systematic study of some structural and electronic properties for the HTS CaLaBaCu₃O₇. We found that theoretical structural parameters are 99% in agreement with experimental reports for CaLaBaCu₃O₇[4].

2. Calculation Method

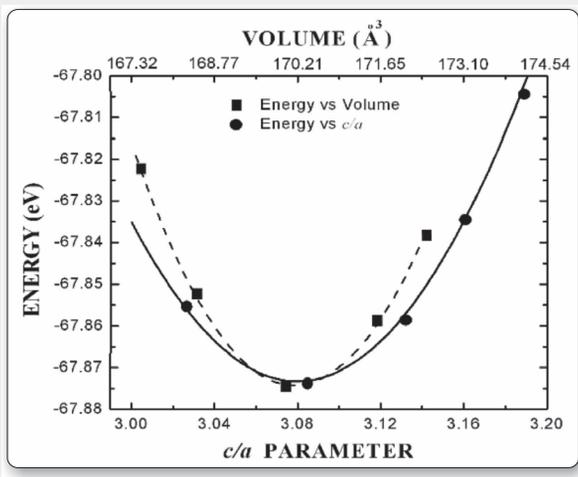
We use the wien2k [5], which is a program based on Density Functional Theory (DFT) and that allows to perform electronic structure calculations of crystalline solids. The wien2k works with the full-potential (linearized) augmented plane-wave (LAPW) + local orbital (lo) method [6], which is the most accurate for band structure calculations. The exchange correlation potential can be treated using several approximations in the framework of local density approximation (LDA) and the generalized gradient approximation (GGA) [7]. This potential considers the difference between the electronic densities for the two distinct spin orientations. The self-consistent calculations are considered to be convergent when the total energies of two successive iterations agreed within 10^{-4} Ry. By searching

the energy minimum, we have optimized the unitary cell volume and structural Oxygen atomic position. From volume, the lattice parameter a is easily found. The muffin-tin radiuses used (in Å) were 2.20, 2.20, 2.25, 1.90 and 1.50 for Ca, La, Ba, Cu and O respectively. $RMT \cdot K_{max} = 9.5$. We used 196 k-points over the irreducible Brillouin zone and the maximum angular momentum inside the muffin-tin sphere was $l=10$.

3. Crystal and Electronic Properties

We performed the minimization of energy as a function of volume and c/a lattice factor, as shown in figure 1. Dashed line represents the fitting of calculated squared points (energy as a function of volume) to the Murnaghan State Equation [8]. Each one of the round points is an individual calculation (energy as a function of c/a) and the continuous line corresponds to a polynomial of grade two which was obtained by the least-square fitting method [9]. The minimum energy (-67.873 eV) is obtained for $c/a=3.08$ and $Volume=170.479 \text{ Å}^3$. The lattice parameters obtained by this methodology were $a=3.811 \text{ Å}$ and $c=11.738 \text{ Å}$.

Fig. 1. Energy as a function of volume (dashed line) and c/a parameter of primitive cell (continuous line) for CaLaBaCu₃O₇. The c/a line corresponds to a parabola of degree 2, while the volume line represents the fitting to the Murnaghan's state equation. Continuous line was obtained by the least-square method.



Densities of states for the CaLaBaCu₃O₇ perovskite were calculated by using the lattice parameter obtained from the energy minimization. Figure 2 shows the structure of CaLaBaCu₃O₇, which was considered for calculations.

Fig. 2. Tetragonal crystalline structure of CaLaBaCu₃O₇ superconductor perovskite, with lattice parameters $a=3.811 \text{ Å}$ and $c=11.738 \text{ Å}$.

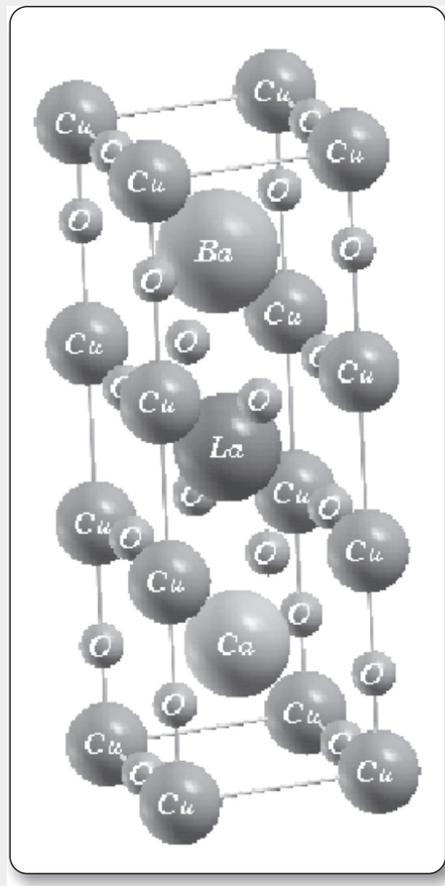
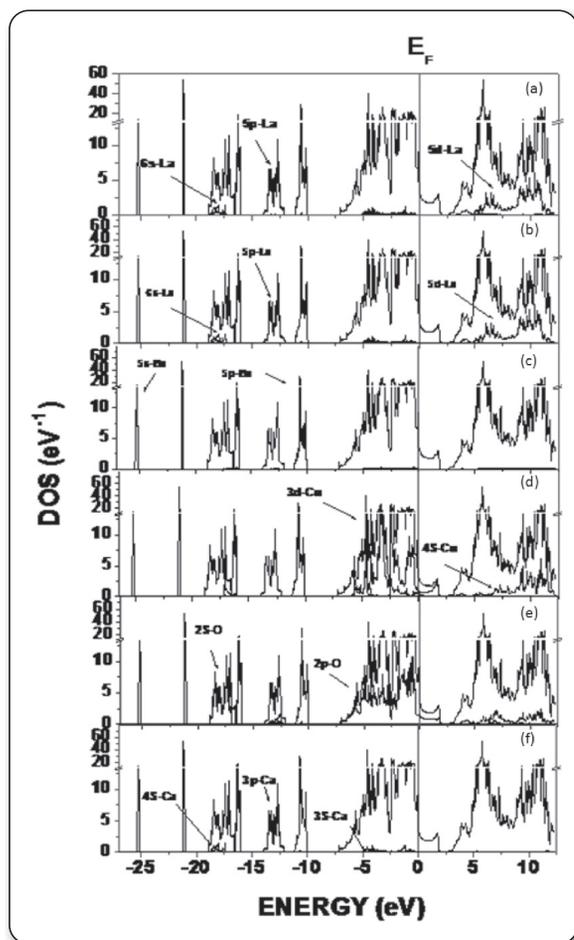


Figure 3 exemplifies the electronic states calculated for the system, as follows: (a) represents total density of states; (b), (c), (d), (e) and (f), correspond to partial contributions of La, Ba, Cu, O and Ca atom orbital, respectively. Fermi level has been choice as energy reference.

As observed in figure 3a, valence band contain a variety of sub-bands. One of more relevant sub-band evidenced as a high and strait peak, is strongly localized and situated deep into the valence band at $E=-25 \text{ eV}$. This band has principally contribution of

Barium 6s orbital (figure 3c). A second energy region, between -19 eV and -17 eV, is majority constituted by Oxygen 2s orbital and insipient contributions of Calcium 3s, 4s, 3p, Lanthanum 5p, 6s and Copper 4s states, as observed in figure 3.

Fig. 3. Total and partial density of states for CaLaBaCu₃O₇: (a) total density of states; (b) Lanthanum, (c) Barium, (d) Copper (e) Oxygen and (f) Calcium partial contributions to the density of states. E_F represents the Fermi level.

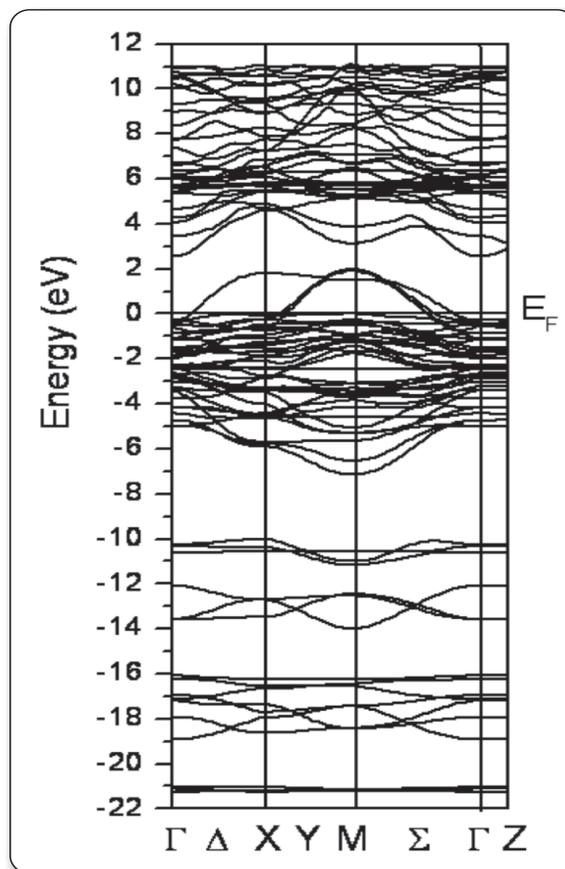


Third sub-band is found from -14 eV up to -12.5 eV. This energy regime is particularly conformed by Lanthanum 5p and Calcium 3p orbital, with a minority contribution of Oxygen 2s and 2p orbital. Fourth energy region is situated at -10 eV and it is characterized by the presence of a high and very strait peak of Barium 5d orbital. This result corresponds to strongly localized valence electrons. Fifth sub-band is located between -5 eV and 0 eV, close to the Fermi level. This is essentially

conformed by of Copper 3d and Oxygen 2p orbital, but minor contributions of Copper 4s, Calcium 3s, 3p, 4s and Lanthanum 5p, 5d, 6s states are present. Immediately above Fermi level, in the conduction band, contributions of Oxygen 2p, Copper 3d, 4s orbital are observed in figure 3.

Approximately for 2.5 eV, inside the conduction band, a energysub-gap is identified. The intermediate regime of conduction band contains principal contributions of Lanthanum 5d and Oxygen 2p orbital. A minor density is formed by Copper 4s, 3d, Oxygen 2s and Lanthanum 5p orbital. Far the Fermi level (approximately 10 eV) relevant contributions of Copper 4s, Lanthanum 5d, Oxygen 2s, 2p states are recognized on figure 3.

Fig. 4. Band energy structure for CaLaBaCu₃O₇. Conduction bands correspond principally to Copper 3d, 4s and Oxygen 2p orbital.



Results of energy band calculations are showed in figure 4. Close to the Fermi level, we clearly identify two conductor bands,

which correspond to Copper $3d$, Copper $4s$ and Oxygen $2p$ orbital. Valence band has minor contribution of Calcium and Lanthanum orbital. As observed in figure 4, Copper $4s$ and Lanthanum $5d$ orbital dominate above and far the Fermi level. It is evidenced in figures 3 and 4 that Barium, Calcium and Lanthanum bands are localized far (below and above) the Fermi level, which suggest that this elements contribute to stabilize the crystalline structure, as notice for other authors for YBa₂Cu₃O₇ material [10]. Close to Fermi level main contributions are due to hybridization between Copper $3d$ and Oxygen $2p$ orbital. Presence of Copper and Oxygen states in these bands, close to the Fermi level, has relevance into the framework of theoretical models, which suggest that Cooper pairing in high temperature superconductors has place into the Cu-O₂ structural planes [11].

4. Conclusions

DFT calculations for CaLaBaCu₃O₇ perovskite material were carried out by the FP-LAPW method. We notice that this is the first report of electronic structure for the CaLaBaCu₃O₇ material. Analysis of structural parameters was performed by minimization of energy with the volume of unitary cell. Calculated values of lattice parameters are in agreement with experimental reports between 99 %. The density of states shows a metallic behavior with unoccupied orbital above at Fermi level. On the other hand, no energy gap was observed through the Fermi level, because this calculation was performed without considering the superconducting phase, e.g., was studied for the normal state. From the analysis of density of states we can to affirm that close to the Fermi level, for both valence and conduction bands, the principal contributions correspond to hybridization of Oxygen $2p$ and Copper $3d$ orbital. These results suggest that ordering of Cu and O elements in the Cu-O₂ planes has relevance for the superconducting properties.

Acknowledgments

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