

# PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>: band structure, optical conductivity and apical oxygen displacement

F. Puch\* and R. Baquero<sup>+</sup>

Department of Physics, CINVESTAV.  
Apdo. Postal 14-740, 07000 México, D.F.

In this paper we present briefly the result of a tight-binding parametrization of the electronic band structure of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. We use it to calculate the normal state optical conductivity. We look further at the longly discussed problem of a possible displacement of the apical oxygen, O(4) in the standard notation, from its theoretical position. There is no consensus on whether this displacement takes actually place or not. We calculate the effect of the different possible displacement on the density of states near the Fermi level, and on the low frequency optical conductivity where we find measurable differences.

En este artículo presentamos brevemente el resultado de una parametrización de amarre fuerte de la estructura electrónica de bandas del PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. Usamos esto para calcular la conductividad óptica del estado normal. Profundizamos en el problema largamente discutido de un posible desplazamiento del oxígeno apical, O(4) en la notación estándar, de su posición teórica. No existe consenso si este desplazamiento existe o no. Calculamos el efecto de los diferentes posibles desplazamientos sobre la densidad de estados cerca del nivel de Fermi, y sobre la conductividad óptica en bajas frecuencias donde encontramos diferencias apreciables.

PACS: 74.25.Gz, 74.25.Jb, 74.72.Bk

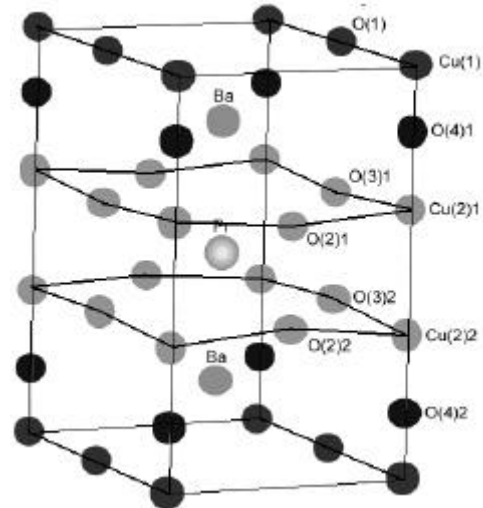
## 1. Introduction

There are very few calculations [1,2] of the electronic band structure of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> in the literature. Superconductivity in this material is interesting since Pr is a magnetic atom. If it would act as Y in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, no holes would be left in the CuO<sub>2</sub>-plane and therefore PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> should not superconduct. This is because, as it is believed, the holes form the Cooper pairs in the CuO<sub>2</sub> planes in high-Tc superconductors (HTSC). Most probably, PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> differs, in several aspects from YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. First, because depending on the way the samples are produced, PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> does or does not become superconducting [3-6]. Second, because the Pr atom could act with a different valence when the sample becomes superconducting or when it does not [1]. Third, because it is not clear whether the Cooper pairs form on the chains rather than (or in addition to) the CuO<sub>2</sub>-planes [7]. Furthermore, similarly as in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, the exact equilibrium position of the apical oxygen (O(4) in the standard notation) atom within the unit cell could differ from the theoretical one. As it is well known for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, a group at Los Alamos [8] found that O(4) atom not to be in its theoretical position in the unit cell, and advances the hypothesis that the local potential is anharmonic. The group of Cardona does not agree on that O(4) is out of its theoretical position at equilibrium [9].

The crystal lattice structure of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is presented in Fig. 1. The theoretical position of all the atoms is shown there as well. The O(4) atom could play an important role in the superconducting state of HTSC. *Polarization-dependent O1s and Cu2p near edge x-ray absorption spectroscopy* experiments on Y<sub>1-x</sub>Ca<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> monocrystals by Merz *et al* [10] and by Nücker *et al* [11], allowed them to conclude that the superconducting state

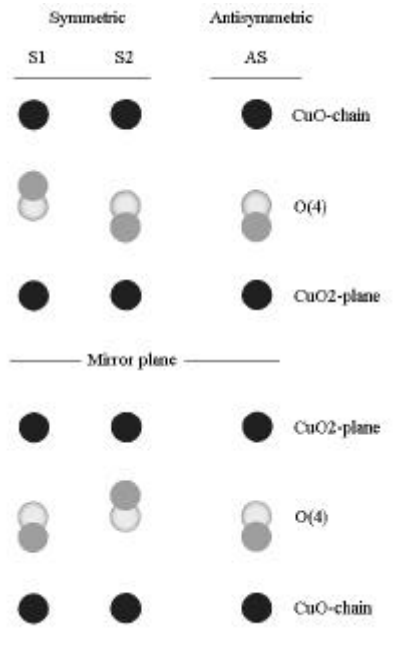
does not take place unless holes are present at O(4) sites irrespective of the number of holes in the CuO<sub>2</sub> planes.

To address the problem in PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> we have attempted a tight binding parametrization. Since the Pr atom can act with different valences, we have studied the various possibilities in our calculation. Here, we assume a valence for the Pr atoms in agreement with the formation of holes on the CuO<sub>2</sub>-plane. Thus, we present a modeled description of the normal state of a PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> sample that does become superconducting in a way similar to that of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. The detailed analysis of this calculation is



**Figure 1.** The electronic structure of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. The 13 atoms that form the unit cell are labeled for clarity. We do not consider the Ba atoms in the tight-binding calculation since their contribution is very far away from the Fermi level and does not influence the final result. We took into account 11 atoms, one CuO-chain atoms: O(1) and Cu(1), two O(4) apical atoms, two CuO<sub>2</sub>-planes atoms composed by O(2), O(3) and Cu(2) atoms each, and one Pr atom.

\* e-mail: fpuch@fis.cinvestav.mx, <sup>+</sup>rbaquero@fis.cinvestav.mx



**Figure 2.** The three different displacement of the apical oxygen O(4) that we have considered. Two of these are symmetric (S1 and S2) and one antisymmetric (AS). The theoretical position (clearest circles) of the O(4) atom is shown in each case for the seek of clarity.

reported elsewhere [12].

In this work we use our just mentioned [12] result to calculate the normal state optical conductivity,  $\sigma_{\text{opt}}(\hat{u})$  in several cases of interest. First, we consider the O(4) atom at its theoretical position. We will refer to this situation as the theoretical one (T). Then we do the same calculation but considering various displacements of the O(4) atom. The amount that we let displace the equilibrium position of the O(4) atoms from their theoretical one is consistent with the findings of *Los Alamos* group [13-15] for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , in all the cases considered. Actually they found two possible equilibrium positions for the O(4) atom which they associate to a double potential well on that site. The distance between the wells vary with the temperature from 0.13 Å at 10 K to 0.02 Å around the critical temperature  $T_c$  [15]. The use of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  data is justified here because the O(4) atom is surrounded by the same nearest neighbouring atoms in both  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{PrBa}_2\text{Cu}_3\text{O}_7$ .

We divide the displacements into two kinds, *i.e.*, the ones that do not violate symmetry and the ones that do so. An O(4) atom lies in between one  $\text{CuO}_2$ -plane and a CuO-chain (see Fig. 1). A symmetric displacement would occur if two consecutive O(4) atoms are moved towards the nearest CuO-chain (S1) or both are moved away from it (S2). We call it symmetric because such displacements do not violate the mirror symmetry around the plane parallel to the  $\text{CuO}_2$ -plane that contains the Pr atom (the M-plane). There is also another kind of displacement, which occurs when all the O(4) atoms are moved in the same direction in the whole sample. In this case, the mirror element of symmetry just described is lost. We refer to such a displacement as antisymmetric (AS). We illustrate this point in Fig. 2.

Notice that for the calculation of the antisymmetric case we need to double the unit lattice since two consecutive chains are not equivalent anymore. In this case, the interaction between the O(4) atom and the chain atoms is different on each side of the M-plane since their relative distance changes.

Our calculation allows us to pinpoint to differences in the low frequency normal state optical conductivity,  $\sigma_{\text{opt}}(\hat{u})$ , that might contribute to further analyze and to settle up the equilibrium position of the O(4) atom in this superconducting perovskites.

## 2. Calculations

Since there are several aspects of  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  that are not yet settled, as the actual Pr valence and its exact position in the cell, a tight-binding approach seems very appropriate for this kind of calculation. Out of theoretical equilibrium positions are easily dealt with in a tight-binding approach and the results are meaningful though approximate. We have obtained the electronic band structure of  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  from the diagonalization of a tight-binding hamiltonian [12] that describes 11 atoms in the unit cell (Ba atoms were excluded since their contribution near the Fermi level is not expected to be important). Our hamiltonian depends on 91 tight-binding parameters. They were calculated following the formula by Harrison [16]. Some were refined using the available information [2,12]. This is the input to the optical conductivity calculation.

Further, we used the tetrahedral method [17,18] to perform the integration over the First Brillouin zone (FBZ). We took 32 points on each axis of the reciprocal space to integrate on 1/8th of the FBZ. We obtained in this way the density of states (DOS) with the aim to compare it to other calculations and models published in the literature [1,2]. It also allowed us to see the influence of each displacement has on the DOS around the Fermi energy ( $E_F$ ) [12].

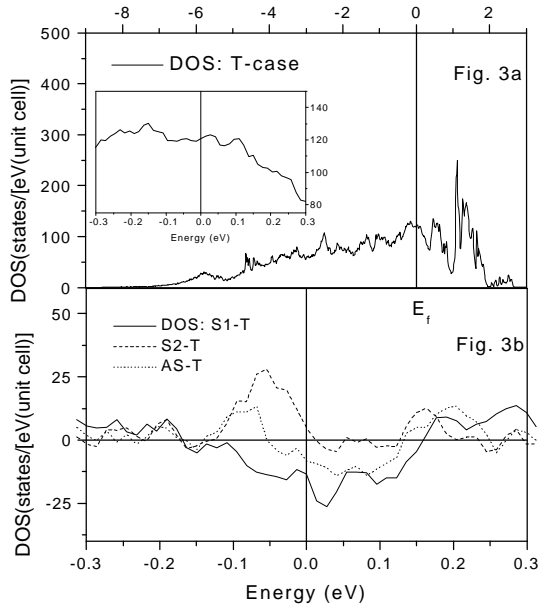
To calculate the optical conductivity,  $\sigma_{\text{opt}}(\hat{u})$ , we used the well known Kubo-Greenwood formula [19].

## 3. Results

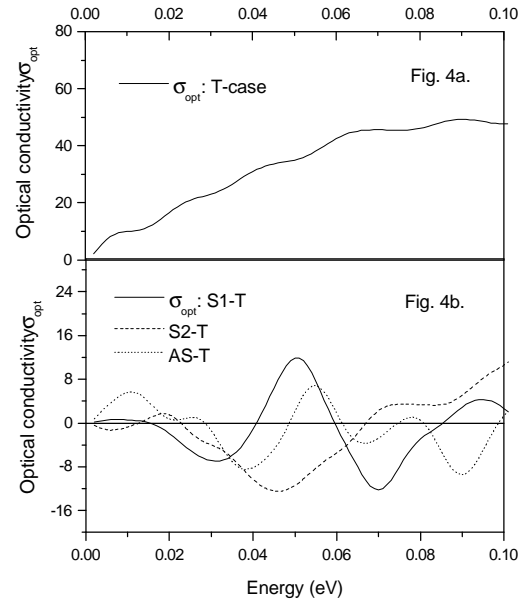
We present here our result on the influence of hypothetical displacements of the apical oxygen O(4) atom from its theoretical equilibrium position in the unit cell. We consider three different possible displacements. They are described above in the text. We labeled them S1, S2 and AS. See Fig. 2. We will show the influence it has on the density of states and on the optical conductivity. We will show the difference with respect to the theoretical case (T-case) where the O(4) atom lies at its theoretical equilibrium position according to the symmetry group perovskites belong to.

### 3.1 The density of states

Our result for the DOS is shown in Fig. 3. We present there the DOS in the T-case around  $E_F$ , Fig. 3a, so that a



**Figure 3.** We show in the upper part (a) the total density of states (DOS) for PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> when the O(4) atom is at its theoretical position (T-case, see text). In the insight we show the details of it in the region of 300 meV from the Fermi energy. In the lower part (b), we show the differences from the theoretical case of the DOS for each of the displacements under study. The differences are noticeable.



**Figure 4.** The optical conductivity  $\delta_{opt}(\tilde{u})$ . The theoretical case (T-case)(when the O(4) atom is at its theoretical position) is presented in the upper part (a). In the lower part (b) we present the difference from the T-case of  $\delta_{opt}(\tilde{u})$  for the different cases considered. The differences are noticeable. It is interesting that in the S2-case that a small gap of 15 meV seems to open at very low energies (See text).

clear comparison with other calculations can be made. At the  $E_F$ , the total DOS is about 120 states/spin/atom/eV. This density is influenced in an important and different way by each of the displacements considered. In Fig. 3b we show the difference in the DOS with respect to the T-case, for the S1 displacement (curve 1), the S2 (curve 2) and the AS one (curve 3). The differences are clear. In Table 1 we show how the DOS at  $E_F$  changes in composition in the different situations. In all the cases considered, the electronic states associated with atoms on the CuO<sub>2</sub>-planes, contribute the most. Nevertheless a density that oscillates around 35% of the states contributing at  $E_F$ , does come from other sites of the sample. This is an important point since Cooper pairs were reported to form also on the chains [7] in the superconducting state of Y<sub>1-x</sub>Pr<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

### 3.2 The optical conductivity

It is of importance to settle the point on the actual experimental position of the O(4) atom in PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. To

**Table 1.** We show different contributions to the density of states (DOS) at the Fermi level ( $E_F$ ) when the equilibrium position of the O(4) atom is displaced in the different situations (See text). The first row is the total DOS at  $E_F$  in units of states/atom/eV/spin. In the others rows we quote the percentage contributions to the total DOS in each case.

	T	S1	S2	AS
<b>Total DOS</b>	120.7	107.2	125.5	112.4
<b>Pr</b>	5.5	5.9	5.1	5.6
<b>Chain</b>	21.7	18.8	25.2	21.7
<b>Planes</b>	58.1	59.1	51.4	56.0
<b>Apical oxygen</b>	13.4	12.6	15.7	12.3

that purpose it is suitable to accumulate more results accessible to experimental verification in cases where the different situations manifest themselves in a distinguishable way. Optical conductivity is an experiment that can be done with high accuracy. In this sense we present the result of the influence of changes in the theoretical equilibrium position of the O(4) atom in the optical conductivity,  $\delta_{opt}(\tilde{u})$ . We begin again to show the T-case,  $\delta_{opt}^T(\tilde{u})$ , so that comparison with other authors work can be made easily. It is shown in Fig. 4a. In Fig. 4b we present differences that we find in each case. The result is that clear differences do appear in the optical conductivity,  $\delta_{opt}(\tilde{u})$ , which could be confronted to an experiment as to help setting the actual position of the O(4) atom. Unfortunately, no experiment on the  $\delta_{opt}(\tilde{u})$  for PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> known to us exists in the literature at present.

The first thing to notice in the normal state  $\delta_{opt}(\tilde{u})$  is that the different situations give rise to clear and measurable differences. This is clear from fig. 4b, *i.e.*, in principle an experiment could add some information. We call particularly attention to the fact the S2-T curve seems to indicate the existence of a small gap in the low frequency optical conductivity. This gap is measurable and could decide at least in part whether the displacement actually exists or not.

### 4. Conclusions

We have calculated the density of states for PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> using a tight-binding technique. We have repeated the calculation with the *ab initio* WIEN98 code and use it to

refine our tight-binding parameters so that the bands around the Fermi energy are very well fitted of the *ab initio* calculation. The final result is very good.

We have addressed the problem of the actual position of the O(4) atom by considering three possibilities for the equilibrium position of this atom. Two of them do not violate the symmetry of the group and one does. We have used our tight-binding description to determine the influence that the displacement of the O(4) atom has in the DOS and, in particular, around the Fermi energy. We find neat differences in intensity and composition. We have further calculate the normal state optical conductivity to establish results that can be confronted to an experiment. Here as well the differences are neat and measurable. We found that when the O(4) atom is displaced towards the CuO<sub>2</sub>-plane a low energy gap seems to form in the optical conductivity. This result is particularly interesting since the experiments are done with enough accuracy to establish whether this gap exists or not.

## References

- [1] M. Tagami, M. Sumida, Ch. Krauns, Y. Yamada, T. Umeda, and Y. Shiohara, *Physica C* **250**, 240 (1995).
- [2] David. J. Singh, *Phys. Rev. B* **50**, 4106 (1994).
- [3] L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, *Nature* **328**, 604 (1987).
- [4] H. B. Radousky, *J. Mat. Res.* **7**, 1917 (1992).
- [5] H. A. Blackstead, D. B. Chrisey, John D. Dow, J. S. Horwitz, A. E. Klunzinger, and D. B. Pulling, *Physica C* **235**, 1539 (1994).
- [6] H.A. Blackstead, D. B. Chrisey, John D. Dow, J.S. Horwitz, A. E. Klunzinger, and D. B. Pulling, *Phys. Lett. A* **207**, 109 (1995).
- [7] Z. Homonnay, Z. Klencsár, V. Chechersky, Gy. Vankó, M. Gál, E. Kuzmann, S. Tyagi, J.-L. Peng, R. L. Greene, A. Vértes, and A. Nath, *Phys. Rev. B* **59**, 11596 (1999).
- [8] A. R. Bishop, R. L. Martin, K. A. Müller, and Tešanoviã, *Z. Phys. B* **76**, 17 (1989).
- [9] C. Thomsen, and M. Cardona, *Phys. Rev. B* **47**, 12320 (1995).
- [10] M. Merz, N. Nücker, P. Schweiss, S. Schuppler, C. T. Chen, V. Chakarian, J. Freeland, Y. U. Idzerda, M. Kläser, G. Müller-Vogt, and Th. Wolf, *Phys. Rev. Lett.* **80**, 5192 (1998).
- [11] N. Nücker, M. Merz, P. Schweiss, E. Pellegrin, S. Schuppler, Th. Wolf, V. Chakarian, J. Freeland, Y. U. Idzerda, M. Kläser, G. Müller-Vogt, G. Er, S. Kikkawa, and G. Liu, *J. Supercond.* **12**, 143 (1999).
- [12] F. Puch, Master Thesis (unpublished); F. Puch, A. Rubio-Ponce, and R. Baquero (to be published).
- [13] Steven D. Conradson, Ian D. Raistrick, Alan R. Bishop, *Science* **248**, 1394 (1990); J. Mustre de Leon, S. D. Conradson, I. Batistia, and A. R. Bishop, *Phys. Rev. Lett.* **65**, 1675 (1990).
- [14] P. G. Allen, J. Mustre de Leon, S. D. Conradson, and A. R. Bishop, *Phys. Rev. B* **44**, 9480 (1991).
- [15] J. Mustre de Leon, S. D. Conradson, I. Batistia, A. R. Bishop, I. D. Raistrick, M. C. Aronson, and F. H. Garzon, *Phys. Rev. B* **45**, 2447 (1993).
- [16] Walter A. Harrison, *Electronic structure*, first edition (W. H. Freeman and Company, San Francisco, 1980).
- [17] D. J. Chadi, and Marvin L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- [18] G. Gilat, and N. R. Bharatiya, *Phys. Rev. B* **12**, 3479 (1975)
- [19] Walter A. Harrison, *solid state theory*, first edition (Dover Publications Inc, New York, 1979).