**Rapid Research Note**

**The Influence of Pr$_{\text{Ba}}$ Disorder on the Electronic Structure of PrBa$_2$Cu$_3$O$_7$**

M. Łuszczek$^1$ and R. Laskowski

Faculty of Applied Physics and Mathematics, Technical University of Gdańsk, G. Narutowicza 11/12, 80-952 Gdańsk, Poland

(Received January 17, 2002; in revised form February 18, 2002; accepted February 18, 2002)

Subject classification: 71.23.An; 74.25.Jb; 74.72.Jt; S10.15

**Introduction** PrBa$_2$Cu$_3$O$_7$ (Pr123) is a very special member of the R123 (R = Y or rare-earth element) family of high-$T_c$ superconductors. It is isostructural to the other R123, but when the material is granular, it normally exhibits neither metallic nor superconducting properties on the macroscopic scale, and a high Néel temperature. Only recent studies of crystalline R123 show bulk superconductivity and a low Néel temperature [1]. It was also shown that superconductivity could be introduced to the as-grown non-superconducting Pr123 single crystals by the use of the sophisticated post-growth process reducing the Pr:Ba off-stoichiometry [2].

Some interesting models, such as e.g. magnetic pair breaking, hole filling, carrier localization, Pr$_{4f}$–O$_{2p}$ hybridization, have been proposed to explain the phenomena but the understanding of the mechanism responsible for the suppression of superconductivity in this system is still insufficient. Recently it has been argued that Pr at the Ba-site (Pr$_{\text{Ba}}$) and not the R-site (Pr$_{\text{R}}$) destroys the superconductivity by the large magnetic moment of Pr since the superconducting carriers were first proposed to occupy the vicinity of the chains [3] but more recently have been located in the BaO layers [4]. The purpose of the present work is to study the band structure of Pr123 with Pr$_{\text{Ba}}$ disorder in the context of the suppression of superconductivity.

**Methodology** In order to examine the influence of Pr on Ba-site substitution on the electronic properties of Pr123 we have performed self-consistent spin-polarized electronic structure calculations within the generalized gradient approximation (GGA) using a local orbital extension of full-potential linearized augmented plane wave (LAPW) method [5]. The core and valence states were treated self-consistently, the former relativistically in an atomic-like approximation and the latter scalar relativistically with spin–orbit interactions included in a second-variational procedure. The Pr 4f$^2$ states were treated as “open core” due to their strongly localized character. Self-consistency was obtained using a set of 32 $k$ points in the irreducible wedge of the Brillouin zone.

The rare-earth and Ba sites originate from the same crystallographic sites of the distorted (R,Ba)CuO$_3$ perovskite. Thus, as a first approach we simulated the Pr$_{\text{Ba}}$ sublattice defects by exchanging Pr and one of Ba atoms in the unit cell, i.e. locating magnetic Pr in the vicinity of chains without “loosing” the 123 stoichiometry of the system. The obtained structure is denoted further in the text as Pr123*. Next, the geometry optimization was carried out by the use of very efficient pseudopotential method [6], exploiting the basis set of plane waves and standard Mankhorst and Pack $k$ mesh generation procedure, to obtain the minimum energy for this system. Assuming the high mobility of oxygen atoms reported for this group of compounds we let the plane and chain oxygen atoms move while the positions of Cu atoms were fixed. This allowed us to use the same experimental cell parameters either for Pr123 or Pr123* because the cell volume was identical in both cases. Finally, the as-prepared Pr123*, with the flattened CuO$_2$ plane located between two Ba atoms and chain O(4) shifted slightly towards Ba, was taken for precise LAPW electronic structure calculations.

**Results** In Fig. 1 we compare the energy bands of Pr123 and Pr123*. The results obtained for perfect Pr123 are generally consistent with the previously reported calculations [7–9]: the metallic...
character of the system is visible with the dominant Cu(1)3d–O(4)2p chain- and Cu(2)3d–O(2,3)2p plane-related bands crossing the Fermi level $E_F$. One can also notice evident dispersion of $E(k)$ in the $x$ and $y$ direction responsible for two-dimensional character of the bands. We found that the high-lying bands exhibit mainly Pr $5d$ and Ba $4d$ character and most of the states in the valence band (VB) below $E_F$ are chain-derived. The strong spin-splitting up to $\sim 0.5$ eV was observed, as well, what is almost ten times greater than obtained by the use of linear muffin-tin orbitals (LMTO) method with atomic sphere approximation (ASA) [7] but less than that previously found by LAPW method with the 4f treated as band states [8] or LMTO-ASA within local spin density approximation including on-site Coulomb interaction (LSDA+U) [9]. Noteworthy, there was no reported significant splitting of bands for the good superconductor Gd123 [7] although Gd possesses a much stronger magnetic moment than Pr does.

As could be seen from Fig. 1 the conduction bands (CB) in Pr123* are shifted downwards by about 3 eV and the upper part of VB consists predominantly of Pr states whereas the “core” remains practically unchanged.

The structure of VB in Pr123 and Pr123* could be studied in detail from the total density of states (DOS) characteristics which are presented in Fig. 2. It is worth noting that the values of DOS at $E_F$ are comparable for both the perfect Pr123 and disordered Pr123*.

It appears from the atomic-projected DOS that the strong spin-splitting in Pr123 affects mostly chain-derived Cu(1)–O(4) bands and, additionally, apical O(1) sites. This could indicate the appearance of enhanced effective magnetic moment in the vicinity of chains. On the contrary, in the
case of structure with magnetic Pr on Ba site the spin-splitting reflected in the site-decomposed DOS is only marginal.

**Conclusions**  The strong spin-splitting of band structure observed in Pr123 could be treated as response to the internal magnetic field produced by exchange interactions rather than the strongly localized Pr 4f magnetic moment. The apparent large magnetic susceptibility of Cu(1), O(4) and O(1) could lead to generation of an effective magnetic moment located predominantly in the chain layers. This would imply that, if the superconductivity is chain-originated, pair breaking could occur due to effective magnetic interactions. On the other hand, the Pr_{Ba} disorder suppresses this spin-splitting without reduction of DOS at \( E_F \).

The further research should be aimed at studying “super-cell” structures simulating oxygen defects which could be provoked by Pr_{Ba} disorder. The investigations of such systems are currently in progress.

**Acknowledgements**  This work was supported by State Committee for Scientific Research (grant No. 2P03B10619). All the calculations were performed at Academic Computer Center in Gdańsk (TASK).

**References**


Electronic structure of CeBa$_2$Cu$_3$O$_7$

M. Łuszczek$^*$ and R. Laskowski

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, G. Narutowicza 11/12, 80-952 Gdańsk, Poland

Received 6 March 2003, revised 12 May 2003, accepted 23 May 2003
Published online 29 July 2003

PACS 74.72.–h;74.62.D

The linearized augmented plane wave (LAPW) method was used for spin-polarized self-consistent electronic structure calculations of CeBa$_2$Cu$_3$O$_7$ (not synthesized as a single phase yet) and compared with three other members of the ReBa$_2$Cu$_3$O$_7$ (denoted as Re123) family of compounds: Y123 (superconducting), Nd123 (superconducting) and Pr123 (potentially-superconducting). The obtained band structures are qualitatively similar. We hypothesize that the spin-split band structure observed in Pr123 and Ce123 could indicate the potential off-stoichiometry, substitutional defects and as a consequence the suppression of superconductivity in the former, and the failure of single phase synthesis in the last system.

$^*$ Corresponding author: e-mail: maclu@mif.pg.gda.pl, Phone: +48 58 347 10 95, Fax: +48 58 347 28 21

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

The ReBa$_2$Cu$_3$O$_7$ (Re = Y or rare-earth element) family of compounds — denoted as Re123 hereafter — has become one of the most popular among superconductivity researchers in the last decade. The typical Re123 compound is a 90 K superconductor with orthorhombic crystal structure when oxygenated, however, there are some intriguing exceptions, that is, Pr123, Ce123, Tb123 and Pm123.

Pr123 is perhaps the most curious member of the Re123 family of high-$T_c$ superconductors. It is isostructural to the other Re123, but when the material is granular, it normally exhibits neither metallic nor superconducting properties on the macroscopic scale, and a high Néel temperature. Only recent studies of crystalline Re123 show bulk superconductivity and it has a low Néel temperature [1]. It was also shown that superconductivity could be introduced to the as-grown non-superconducting Pr123 single crystals by the use of the sophisticated post-growth process reducing the Pr and Ba off-stoichiometry (what means that the Pr:Ba molar ratio is close to nominal 1:2) [2]. Some interesting models, such as e.g. magnetic pair breaking, hole filling, carrier localization, Pr$_{4f}$–O$_{2p}$ hybridization, have been proposed to explain the phenomena but the understanding of the mechanism responsible for the suppression of superconductivity in this system is still insufficient. Recently it has been argued that Pr at the Ba-site ($P_{PrB}$) and not the Re-site ($P_{PrR}$) destroys the superconductivity by the large magnetic moment of Pr since the superconducting carriers were first proposed to occupy the vicinity of the chains [3] but more recently have been located in the BaO layers [4]. The $ab$ initio calculations of Pr123 with $P_{PrB}$ [5] seem to support this concept. Despite the great number of papers published on this controversial subject, there is no common agreement concerning the structural and physical properties of Pr123 and it still waits for coherent theoretical description.

Ce and Tb do not form a single “123” phase. Interestingly, Ce could be introduced to the Y123 lattice and exhibits the some destructiv influence on the superconductivity as Pr does [6]. As far as we
know there are no reported data on the Tb and Pm compound, in the case of Pm probably due to its radioactivity.

The purpose of the present work is to study the band structure of Ce123 (not synthesized as a single phase yet) and to compare with the electronic structures of three other members of ReBa2Cu3O7 family of compounds: Y123 (superconducting), Nd123 (superconducting) and Pr123 (potentially-superconducting).

2 Computational method

The present calculations were performed within the generalized gradient approximation (GGA) using a local orbital extension of the full-potential linearized augmented plane wave (LAPW) method [7]. The electronic structures of Y123, Pr123 and Nd123 systems were calculated using crystallographic data. As mentioned before, single-phase Ce123 has not been synthesized yet, so the hypothetical crystal structure had to be assumed. We chose the lattice parameters of Pr123 because of similar Pr$^{3+}$ and Ce$^{3+}$ ionic radiiues.

The core and valence states were treated self-consistently, the former relativistically in an atomic-like approximation [8] and later – scalar relativistically with spin-orbit interactions included in a second-variational procedure [9]. The Nd 4f$^{3}$, Pr 4f$^{2}$ and Ce 4f$^{1}$ states were treated as "open core" due to their strongly localized character. Self-consistency was obtained using a set of 16 k points in the irreducible wedge of the Brillouin zone and the total energy as a measure of convergence.

3 Results and discussion

The band structures of Y123 and Nd123 are presented in Fig. 1a and b, respectively. The results obtained for Y123 are consistent with the previously calculated band structures of this system [10, 11]. Although, contrary to Y, a Nd atom exhibits magnetic moment due to its 4f$^{3}$ electrons, the electronic structures of Nd123 and Y123 are practically identical and the spin splitting of bands in the Nd compound is very small. The analogous situation was reported for the good superconductor Gd123 (with magnetic Gd introducing 4f$^{7}$ electrons to the system) from spin-polarized calculations performed by the use of linear muffin-tin orbitals method (LMTO) [11]: the obtained band structures of magnetic Gd123 with negligible spin splitting of its bands and non-magnetic Y123 were almost the same.

The calculated band structures of Pr123 and Ce123 (Fig. 1c and d) are qualitatively similar to those obtained for Y123 or Nd123. We found out that in all the cases, the valence bands (VB) consist mostly of Cu(1)$_{dz}^{2}$–O(4)$_{py}$ chain-related and Cu(2)$_{dz}^{2}$–O(2,3)$_{px,y}$ plane-related states. All Re-derived bands have mainly d character and lie far above the Fermi level. It is noteworthy that, the Pr123 and Ce123 exhibit strong spin splittings of their VBs, as large as approximately 0.5 eV. Such an effect was previously supposed to suppress the superconductivity in the Pr123 system because of magnetic pair breaking [11]. In the light of the newest reports, however, the situation seems to be more complicated since some off-stoichiometry appears and Pr$_{Ba}$ substitutional defects occur leading to significant lowering of the splitting (see [5] and references therein). As a consequence the superconductivity disappears.

The density of states (DOS) near the Fermi level $E_F$ is similar for all the examined systems. The total DOS characterisitics of Nd123, Pr123 and Ce123 are shown in Fig. 2. More detailed analysis is possible from the spin-polarized partial (atomic) DOS curves calculated for these systems and presented in Figs. 3, 4 and 5. As could be immediately noticed, in Pr123 and Ce123 systems the largest spin densities (i.e. the difference between densities of spin $\alpha$ and $\beta$) occurs in Cu–O chains (O(4) site) and Ba–O planes (O(1) site), whereas the CuO$_2$ planes are less affected. As a result, this could indicate the appearance of an enhanced effective magnetic moment in the vicinity of chains. Our results are generally in agreement with previously reported partial DOS of Pr123 [11–13] but spin-splitting we obtained is stronger than in Refs. [11, 13].
In our opinion on the basis of the results presented in this work as well as previously reported in the literature, the following working hypothesis could be put forward. The spin splitting of electronic structure, visible in the \textit{ab initio} calculations of ideally stoichiometric \textquotedblright{}123\textquotedblright{} systems, could be, to some extent, a good indicator of potential problems with the stoichiometric composition in the real crystal structure. More precisely, that could mean that stable Re123 materials (even with defects)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The electronic band structures of a) Y123 (superconducting), b) Nd123 (superconducting), c) Pr123 (sometimes-superconducting) and d) hypothetical Ce123. The radii of open circles are proportional to Re \textit{d}-character.}
\end{figure}
Fig. 2 Total density of states (DOS) near the Fermi level $E_F$ for stoichiometric Nd123, Pr123 and Ce123.

Fig. 3 The partial (atomic) density of states (DOS) in Nd123 for spin $\alpha$ (up) and $\beta$ (dn). The Fermi level was put at 0 eV.
Fig. 4 The partial (atomic) density of states (DOS) in Pr123 for spin $\alpha$ (up) and $\beta$ (dn). The Fermi level was put at 0 eV.

Fig. 5 The partial (atomic) density of states (DOS) in Ce123 for spin $\alpha$ (up) and $\beta$ (dn). The Fermi level was put at 0 eV.
should exhibit crystal structure guaranteeing minimal spin splitting in the band structures. If the splitting does not exist (Y123) or is small enough (Nd123, Gd123), the off-stoichiometry is negligible and the level of substitutional defects is low. These compounds are good superconductors. In contrast, poor superconductors (Pr123) exhibit significant off-stoichiometry and high levels of substitutional defects. This minimizes the spin splitting of the system, but, on the other hand, suppresses the superconductivity. The same destructive effect of Pr and Ce on the superconducting Y123 [6] allows one to suspect that either Pr or Ce could generate the same kind of structural changes (defects, distortions) in the crystal “host matrix”. Probably the off-stoichiometry of Ce123 system is larger than in Pr123 and that is why the single “123” phase could not be synthesized in standard way (too large “shift” in the Ce–Ba–Cu–O phase diagram leading to the decomposition).

4 Conclusions

LAPW calculations of stoichiometric Re123 (Re = Y, Nd, Pr, Ce) have been performed. The obtained band structures are qualitatively similar. We hypothesize that the spin-split band structures observed in ideally stoichiometric Pr123 and Ce123 could indicate that the off-stoichiometry in real materials provokes the formation of substitutional defects. As a result the suppression of the superconductivity in Pr123 occurs. It is very likely that in the case of the Ce123 the composition “shift” in the phase diagram is too large to enable the formation of a single Ce123 phase.

All the results presented in this paper should be treated as a first stage study of the correlation between crystal structure and electronic properties of Re123, and more computational work on the other Re123 systems is necessary to corroborate our hypothesis. Further investigations should be aimed to determine the influence of different types of defects on the electronic structure and, especially, the magnetic properties of this class of materials.

Acknowledgements This work have been supported by State Committee for Scientific Research (KBN) under grant No. 2P03B10619. The calculations were performed at Academic Computer Center in Gdańsk (TASK).

References

Z. Zou, J. Ye, K. Oka, and Y. Nishihara, Phys. Rev. Lett. 80, 1074 (1998);
Charge distribution and magnetic interactions in $PrBa_2Cu_3O_7$
with substitutional defects and oxygen disorder:
The ab initio approach

Maciej Łuszczek
Faculty of Applied Physics and Mathematics
Gdansk University of Technology
G. Narutowicza 11/12, 80-952 Gdansk, Poland

Keywords: Superconductivity, $PrBa_2Cu_3O_7$, Ab initio calculations, Defects

Abstract. The augmented plane wave + local orbitals method (APW+lo), within the density functional theory formalism, was used for spin-polarized self-consistent calculations of the 54-atom supercell model of $PrBa_2Cu_3O_7$ with $Pr$-on-Ba-site defect ($Pr_{Ba}$) and the anti-chain $O(5)$ oxygens. Some redistribution of total charge in both the $CuO_2$ planes and $CuO$ chains takes place. The charges of barium and oxygens in the $BaO$ layer remain unchanged when comparing with the stoichiometric system. The changes introduced by the simulated defects affect mostly $O_{p}$ and $Cu_{d}$ shells. Significant difference in occupation of “spin-up” and “spin-down” states is visible in the $Cu(2)$ $d_{x^2−y^2}$ orbital. The $Pr_{Ba}$ defect produces localized magnetic moment in the $BaO$ layer. The enhanced magnetic moments are induced on the $Cu(2)$ sites in the $CuO_2$ planes. In contrary, the magnetic moments of $Cu(1)$ in the $CuO$ chains are practically unaffected.

Introduction

$ReBa_2Cu_3O_7$ ($Re$123) family of high-temperature superconductors ($Re$ stands for rare-earth element substituting for yttrium in the parent $YBa_2Cu_3O_7$ compound) become one of the most popular among superconductivity researchers in the last decade. Typical $Re$123 has critical temperature $T_C \approx 90\,K$ and its crystal structure is orthorhombic when material is oxygenated.

$Pr$123 is perhaps the most extensively investigated member of $Re$123 because of its specific structural and transport properties. It is isostructural to the other superconducting $Re$123 homologues, but, on the other hand, it normally exhibits neither metallic nor superconducting properties on the macroscopic scale and a high Néel temperature, when synthesised by the standard methods [1–9].

The rare-earth and barium sites originate from the same crystallographic sites of the distorted ($Re$, $Ba$)CuO$_3$ perovskite and the potential possibility of $Re$ substitution for $Ba$ occurs. Indeed, there is a strong experimental evidence (Ref. [10] and references therein) indicating that in $Pr$123, as well as in the related $La$123 and $Nd$123 systems, some fraction of $Ba$ sites is occupied by the rare-earth $Re^{+3}$ ions. It was also noticed, that to facilitate such a substitution some anti-chain $O(5)$ oxygens must form to balance charge. It appears that this substitutional defects seem to be crucial for solving the puzzle of the unusual properties of $Pr$123. One could suspect that the imperfect material does not superconduct because it contains too many Cooper pair-breaking centers. Noteworthy, the $Pr^{+3}$ ion is unique because of its large size which allow
praseodymium to occupy Ba sites without the significant lattice distortion (the considerably smaller ions should have difficulty occupying a Ba site in the '123' structure, being too small to efficiently bond to the nearest neighbors).

Despite the great number of papers published on there is still no common agreement concerning the structural and physical properties of Pr123 system. The models assuming non-superconductivity of Pr123 assign its curious behavior to: (i) a hole-filling mechanism due to +4 valence for Pr, causing the reduction of holes in the CuO$_2$ planes by the extra, when comparing with the other Re$^{+3}$ ions in Re123, electrons (in the light of the evidence for the trivalency of Pr on the rare-earth site [11, 12] this explanation seems to be very unlikely), (ii) strong hybridization between Pr4f and plane O2p orbitals, leading to magnetic pair breaking of charge carriers by Pr4f moments or (iii) a hole localization effect, lowering the density and mobility of holes [13, 14]. It is clear, however, that the discovery of the traces of superconductivity in Pr123 system [15–19] makes the situation more complicated and the existing models must be modified [20]. Recently it has been argued that Pr on the Ba site (Pr$_{Ba}$) and not the Re site destroys the superconductivity by the large magnetic moment of Pr since the superconducting carriers were first proposed to occupy the vicinity of the chains [15, 21] but more recently have been located in the BaO layers [22].

To organize the experimental data, the following hypothesis was proposed by Blackstead and Dow [10]. The magnetic rare-earth ions (e.g. Tb) do not degrade the superconductivity when they occupy Re sites because they are distant from the chain layers which are the root of the superconductivity. When the magnetic Re ions (such as Ce, Pr, Nd or actinide Cm) occupy Ba sites, however, they are adjacent to the chain oxygen atoms, which, being under-charged or neutral, can normally provide one or two holes and initiate the superconductivity. But Ba-site Re (Re$_{Ba}$) in the +3 charge state can both magnetically break pairs and fill holes, unlikely any +4 ions on Re sites.

Inspired by the reasoning of Blackstead and Dow we have decided to find out by the ab initio method if Pr on the Ba site could significantly influence the electronic structure and physical properties of Pr123 system. As a first approach, in the previous work we simulated the Pr$_{Ba}$ defects by exchanging Pr and one of Ba atoms in the unit cell, i.e. locating magnetic praseodymium in the vicinity of CuO chains without “loosing” the “123” stoichiometry of the system [23]. Interestingly, taking such a model as an input some spin-splitting in the density of states (DOS) was observed mostly for chain-derived states. We hypothesised that as a consequence some effective magnetic moment, located predominantly in the chain layers, could be generated as well. However, we realized that further calculations were necessary and the model simulating oxygen defects which could be provoked by Pr$_{Ba}$ disorder should be examined. In this work we report on the supercell calculations which should be treated as a next step in the ab initio investigation of the Pr$_{Ba}$Cu$_3$O$_7$ compound.

Methodology

Two models of Pr123 system were prepared: (i) the perfect crystal with the elementary cell of stoichiometric Pr$_{Ba}$Cu$_3$O$_7$ constructed according to crystallographic data and (ii) the defected one with the periodicity described by the $2 \times 2 \times 1$ supercell consisting of four elementary cells with one additional Pr on the Ba site and occupied anti-chain oxygen sites O(5) in the vicinity of the simulated Pr$_{Ba}$ defect (Fig. 1).

The calculations were performed using WIEN2k package [25] which is an implementation of augmented plane wave + local orbitals method (APW+lo) within the density functional theory
Charge distribution and magnetic interactions in $PrBa_2Cu_3O_7$

Fig. 1: The supercell of $PrBa_2Cu_3O_7$ with $Pr_{Ba}$ defect and $O(5)$ disorder in the chain layer. (Graphics generated by XCRYSDEN [24])

<table>
<thead>
<tr>
<th>Atom</th>
<th>Configuration</th>
<th>Core states</th>
<th>Valence states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>$[Xe] 4f^2 5d^1 6s^2$</td>
<td>$[Kr] 4d^{10}$</td>
<td>$4f^2 5s^2 5p^6 6d^1 6s^2$</td>
</tr>
<tr>
<td>Ba</td>
<td>$[Xe] 6s^2$</td>
<td>$[Kr] 4d^{10}$</td>
<td>$5s^2 5p^6 6s^2$</td>
</tr>
<tr>
<td>Cu</td>
<td>$[Ar] 3d^9 4s^2$</td>
<td>$[Ne] 3s^2$</td>
<td>$3p^6 3d^9 4s^2$</td>
</tr>
<tr>
<td>O</td>
<td>$[He] 2s^2 2p^4$</td>
<td>$[He]$</td>
<td>$2s^2 2p^4$</td>
</tr>
</tbody>
</table>

Table 1: Initial electron configuration taken for calculations.

formalism [26]. The APW+lo method expands the Kohn-Sham orbitals [27] in atomic-like orbitals inside the atomic muffin-tin spheres (MT) and plane waves in the interstitial region. The basis set inside each MT sphere is split into core and valence subsets. The core states are treated within the spherical part of the potential and are assumed to have a spherically symmetric charge density totally confined inside the muffin-tin spheres. The valence part is treated within a potential expanded into spherical harmonics. The details of the initial electron configurations taken for our calculations are collected in Table 1.

The MT sphere radii of 2.3 bohr were used for both $Pr$ and $Ba$, whereas 1.8 bohr and 1.55 bohr were applied for $Cu$ and $O$, respectively. A plane-wave expansion with $R_{MT}K_{MAX} = 5$
and $8 \times 8 \times 2$ mesh of $k$-points in the full Brillouin zone were applied for the perfect $Pr123$. The supercell calculations were carried out with $2 \times 2 \times 1$ $k$-sampling and the same value of $R_{MTK_{\text{MAX}}}$. All the calculations were performed utilizing the generalized gradient approximation (GGA) with the potential given by Perdew, Burke, and Ernzerhof [28].

Results and discussion

The main advantage of the applied method is that the wave functions and the charge density can be decomposed into atomic contributions. Furthermore, so called partial charges (with $s$, $p$, $d$ or $f$ character) could be examined for all atoms in the system. These quantities enable us to get some important information concerning the charge distribution in the system.

The values of total charge inside MT spheres in the perfect and the defected $Pr123$ are presented in Table 2. As could be seen, the introduction of the $Pr_{Ba}$ defect and the anti-chain oxygens causes some redistribution of charge in the system. In the case of $Pr$ sublattice the loss of about $0.01 \, e^-$ is observed in the defected system. The $CuO_2$ planes and $CuO$ chains are affected, too. $Cu(2)$ gains about $0.01 \, e^-$ (transfered from $O(3)$ site), whereas $Cu(1)$ losses the comparable amount of charge. This redistribution of charge influences the ionicity of the bonding between $Cu$ and $O$ atoms, namely, ionic character is slightly decreased in the planes and increased in the chains. Also the $O(5)$ MT sphere contains slightly less charge than the $O(4)$ one what could indicate some anisotropy of the bonding in the $CuO_2$ planes. The total charge of $Pr_{Ba}$ is significantly lowered when compared with the $Pr$ in the regular position (the difference of $\sim 0.1 \, e^-$). Noteworthy, the charges of barium and oxygen in the $BaO$ layer remain unchanged.

Partial charges for the perfect and the defected systems are listed in Tables 3 and 4, respectively. It could be noticed that the difference between occupation of the minority and the majority spin states of $Pr$ in the defected $Pr123$ system is slightly lowered. In the case of the $Pr$ on the $Ba$ site, however, the opposite behaviour could be observed. What is more, some

<table>
<thead>
<tr>
<th>Sublattice</th>
<th>Perfect Atom</th>
<th>Charge</th>
<th>Defected Atom</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Pr</td>
<td>55.435</td>
<td>Pr</td>
<td>55.426</td>
</tr>
<tr>
<td>CuO$_2$ (planes)</td>
<td>Cu(2)</td>
<td>27.005</td>
<td>Cu(2)</td>
<td>27.014</td>
</tr>
<tr>
<td></td>
<td>O(2)</td>
<td>6.932</td>
<td>O(2)</td>
<td>6.932</td>
</tr>
<tr>
<td></td>
<td>O(3)</td>
<td>6.937</td>
<td>O(3)</td>
<td>6.926</td>
</tr>
<tr>
<td>BaO (planes)</td>
<td>Ba</td>
<td>52.479</td>
<td>Ba</td>
<td>52.480</td>
</tr>
<tr>
<td></td>
<td>O(1)</td>
<td>6.899</td>
<td>O(1)</td>
<td>6.889</td>
</tr>
<tr>
<td>CuO (chains)</td>
<td>Cu(1)</td>
<td>26.964</td>
<td>Cu(1)</td>
<td>26.949</td>
</tr>
<tr>
<td></td>
<td>O(4)</td>
<td>6.870</td>
<td>O(4)</td>
<td>6.869</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O(5)</td>
<td>6.852</td>
</tr>
</tbody>
</table>

Table 2: Total charge inside MT spheres (in $e^-$) for stoichiometric $PrBa_2Cu_3O_7$ (perfect) and $PrBa_2Cu_3O_7$ with $Pr_{Ba}$ defect and $O(5)$ disorder (defected).
Charge distribution and magnetic interactions in PrBa$_2$Cu$_3$O$_7$

### Partial charges in perfect system

<table>
<thead>
<tr>
<th>Sublattice</th>
<th>Atom</th>
<th>Spin</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Pr</td>
<td>up</td>
<td>0.964</td>
<td>2.604</td>
<td>0.197</td>
<td>1.731</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.961</td>
<td>2.593</td>
<td>0.182</td>
<td>0.199</td>
</tr>
<tr>
<td>CuO$_2$</td>
<td>Cu(2)</td>
<td>up</td>
<td>0.100</td>
<td>3.077</td>
<td>4.299</td>
<td>–</td>
</tr>
<tr>
<td>(planes)</td>
<td></td>
<td>down</td>
<td>0.100</td>
<td>3.077</td>
<td>4.335</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(2)</td>
<td>up</td>
<td>0.773</td>
<td>1.670</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.775</td>
<td>1.703</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(3)</td>
<td>up</td>
<td>0.772</td>
<td>1.672</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.773</td>
<td>1.706</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BaO</td>
<td>Ba</td>
<td>up</td>
<td>0.896</td>
<td>2.276</td>
<td>0.057</td>
<td>–</td>
</tr>
<tr>
<td>(planes)</td>
<td></td>
<td>down</td>
<td>0.896</td>
<td>2.276</td>
<td>0.057</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(1)</td>
<td>up</td>
<td>0.773</td>
<td>1.672</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.773</td>
<td>1.673</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CuO</td>
<td>Cu(1)</td>
<td>up</td>
<td>0.113</td>
<td>3.079</td>
<td>4.285</td>
<td>–</td>
</tr>
<tr>
<td>(chains)</td>
<td></td>
<td>down</td>
<td>0.113</td>
<td>3.079</td>
<td>4.275</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(4)</td>
<td>up</td>
<td>0.774</td>
<td>1.658</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.773</td>
<td>1.656</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 3: Partial charges (in e$^-$) inside atomic spheres for stoichiometric (perfect) PrBa$_2$Cu$_3$O$_7$.

transfer from $d$ to $f$ character in the Pr atom substituting for Ba in the BaO layer is observed what could mean the stronger localization of charge in the Pr$_{Ba}$ defects comparing with the regular Pr site.

One can also see that the changes introduced by the simulated defects affect mostly O$p$ and Cu$d$ shells in the CuO$_2$ planes and CuO chains. This effect is visible especially for the Cu(2)$_d$ states in the planes: the difference between “up” and “down” partial charges increases its value from about 0.04 e$^-$ for the perfect system to 0.17 e$^-$ for the defected one. We found out that these changes are mostly related to $d_{x^2-y^2}$ orbital what implies the potential influence on the two-dimensional in-plane transport properties. Moreover, some transfer of charge from $d$ states to $p$ stats of Cu(1) in the chains was noticed in the supercell calculations but it does not influence the total splitting of spins. The general tendency to increase the disproportion between occupation of states with different spins for all the oxygens was observed in the defected Pr123. On the other hand, the partial charges of Ba do not change significantly.

It should be pointed out at this place that the reported data concerns the charge inside the atomic MT spheres. In the applied computational method, however, some amount of charge is “smeared” in the interstitial region, as well. Fortunately, the used software enables the visualisation of the complete topology of charge in the examined systems. In Figs. 2 and 3 the three-dimensional electron spin density plots (showing the difference between spin-up and spin-down densities) and the corresponding two-dimensional spin maps with the isolines for the (a) CuO$_2$ planes, (b) BaO layers and (c) CuO chains in the perfect and defected Pr123 are presented. As could be seen from Fig. 3 b, Pr$_{Ba}$ defects are the source of the additional strongly localized magnetic moment due to the high on-site density of spin. In Fig. 3 a the high-density peaks on the all Cu(2) sites in the defected Pr123 system indicate strong magnetic interactions
Table 4: Partial charges \((\text{in} \, \text{e}^{-})\) inside atomic spheres for \(PrBa_{2}Cu_{3}O_{7}\) with \(Pr_{Ba}\) defect and \(O(5)\) disorder (defected).

<table>
<thead>
<tr>
<th>Sublattice</th>
<th>Atom</th>
<th>Spin</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Pr</td>
<td>up</td>
<td>0.964</td>
<td>2.606</td>
<td>0.201</td>
<td>1.692</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.961</td>
<td>2.596</td>
<td>0.184</td>
<td>0.216</td>
</tr>
<tr>
<td>CuO(_{2}) (planes)</td>
<td>Cu(2)</td>
<td>up</td>
<td>0.098</td>
<td>3.077</td>
<td>4.237</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.101</td>
<td>3.078</td>
<td>4.405</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(2)</td>
<td>up</td>
<td>0.771</td>
<td>1.652</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.775</td>
<td>1.720</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(3)</td>
<td>up</td>
<td>0.772</td>
<td>1.649</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.776</td>
<td>1.717</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BaO (planes)</td>
<td>Pr(_{Ba})</td>
<td>up</td>
<td>0.955</td>
<td>2.579</td>
<td>0.136</td>
<td>1.916</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.952</td>
<td>2.565</td>
<td>0.118</td>
<td>0.112</td>
</tr>
<tr>
<td></td>
<td>Ba</td>
<td>up</td>
<td>0.896</td>
<td>2.278</td>
<td>0.056</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.896</td>
<td>2.279</td>
<td>0.055</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(1)</td>
<td>up</td>
<td>0.775</td>
<td>1.643</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.776</td>
<td>1.686</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CuO (chains)</td>
<td>Cu(1)</td>
<td>up</td>
<td>0.112</td>
<td>3.094</td>
<td>4.262</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.112</td>
<td>3.094</td>
<td>4.249</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(4)</td>
<td>up</td>
<td>0.778</td>
<td>1.632</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.779</td>
<td>1.667</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O(5)</td>
<td>up</td>
<td>0.784</td>
<td>1.612</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>down</td>
<td>0.785</td>
<td>1.658</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

induced in the CuO\(_{2}\) planes. It is worth to note that the analogous charge density contours of CuO\(_{2}\) planes in Pr123 were also obtained experimentally \([29]\), giving similar results. On the other hand, in the defected system spin densities on Cu(1) sites in the chains remain practically unchanged with the simultaneous change in sign and value of spin on the O(4) sites (compare Fig. 2 c and Fig. 3 c).

The values of magnetic moments determined inside each atomic sphere for both the systems are presented in Table 5. The antiferromagnetic ordering of Cu(1) – Cu(2) sublattice is visible either in the perfect or defected system. The largest relative changes in magnetic moments are observed for Cu(2) from the CuO\(_{2}\) planes where the magnetic moments increase from 0.037 \(\mu_{B}\) up to 0.173 \(\mu_{B}\) when the \(Pr_{Ba}\) defect is present. In contrary, magnetic moments of Cu(1) from the chains do not change. It could be also noticed that magnetic moment of \(Pr_{Ba}\) is higher than that of \(Pr\) in the regular position.

The last thing to be discussed is some discrepancy between the data reported in Ref. \([23]\) and the results presented in this work. Although the magnetic moments were not directly distinguished in the previous work, the largest magnetic interactions were supposed to appear mainly in the CuO chains and not CuO\(_{2}\) planes. That effect was probably due to the limitations of the used model. We should remember that in the former calculations \(Pr\) and one of \(Ba\)
Charge distribution and magnetic interactions in PrBa$_2$Cu$_3$O$_7$

![Figure 2](image1.png)

Fig. 2: The electron spin density (in $e/\text{Å}^3$) in (a) CuO$_2$ plane, (b) BaO layer and (c) CuO chains in perfect Pr123. The high-density peaks arise from (a) Cu(2), (b) O(1) and (c) Cu(1) sites. The 100 × 100 grid corresponds to the $ab$-plane cross-section of one elementary cell (3.86 × 3.93 Å$^2$). See Fig. 1 for details.
Fig. 3: The electron spin density (in $e/\text{Å}^3$) in (a) $CuO_2$ plane, (b) $BaO$ layer and (c) $CuO$ chains in the defected $Pr123$. The high-density peaks arise from (a) $Cu(2)$, (b) $Pr_{Ba}$ and (c) $Cu(1)$ sites. The $100 \times 100$ grid corresponds to $ab$-plane cross-section of four elementary cells ($7.72 \times 7.85 \text{Å}^2$). See Fig. 1 for details.
Table 5: Magnetic moments (in $\mu_B$) inside atomic spheres for stoichiometric $PrBa_2Cu_3O_7$ (perfect) and $PrBa_2Cu_3O_7$ with $Pr_{Ba}$ defect and anti-chain $O(5)$ oxygens (defected).

<table>
<thead>
<tr>
<th>Sublattice</th>
<th>Atom</th>
<th>$\mu$</th>
<th>Sublattice</th>
<th>Atom</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Pr</td>
<td>1.560</td>
<td>Pr</td>
<td>Pr</td>
<td>1.506</td>
</tr>
<tr>
<td>CuO$_2$ (planes)</td>
<td>Cu(2)</td>
<td>-0.037</td>
<td>Cu(2)</td>
<td>-0.173</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(2)</td>
<td>-0.034</td>
<td>O(2)</td>
<td>-0.073</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(3)</td>
<td>-0.035</td>
<td>O(3)</td>
<td>-0.072</td>
<td></td>
</tr>
<tr>
<td>BaO (planes)</td>
<td>Ba</td>
<td>-0.000</td>
<td>Ba</td>
<td>-0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(1)</td>
<td>-0.001</td>
<td>O(1)</td>
<td>-0.044</td>
<td></td>
</tr>
<tr>
<td>CuO (chains)</td>
<td>Cu(1)</td>
<td>0.010</td>
<td>Cu(1)</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(4)</td>
<td>0.002</td>
<td>O(4)</td>
<td>-0.036</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(5)</td>
<td></td>
<td>O(5)</td>
<td>-0.046</td>
<td></td>
</tr>
</tbody>
</table>

Summary

The augmented plane wave + local orbitals method (APW+lo), within the density functional theory formalism, was used for spin-polarized self-consistent calculations of the supercell model of $PrBa_2Cu_3O_7$ with $Pr_{Ba}$-on-Ba-site defect ($Pr_{Ba}$) and the anti-chain $O(5)$ oxygens.

All the presented data indicate that the introduction of the $Pr_{Ba}$ defect and the anti-chain oxygens causes some noticeable changes in the distribution of charge in the system. Some redistribution of total charge in both the CuO$_2$ planes and CuO chains takes place. As a result, Cu(2) in the planes gains about 0.01 $e^-$ whereas Cu(1) in the chains losses the comparable amount of charge. On the other hand, the charges of barium and oxygen in the BaO layer remain unchanged. The changes introduced by the simulated defects affect mostly $O_p$ and Cu $d$ shells. Significant difference in occupation of spin-up and spin-down states is visible especially in the $Cu(2) d_{x^2-y^2}$ orbital.

The spatial distribution of spin was examined. It was shown that $Pr_{Ba}$ defect produces localized magnetic moment in the BaO layer due to high on-site spin density. It appears from the calculations that enhanced magnetic moments are induced on the Cu(2) sites in the CuO$_2$ planes. In contrary, the magnetic moments of Cu(1) in the CuO chains are practically the same as in the stoichiometric Pr123.
We can conclude that the simulated $Pr_{Ba}$ defect with the anti-chain $O(5)$ disorder can modify the charge distribution towards the enhanced magnetic interactions in the $Pr123$ system. It is possible, that this effect could be responsible for the suppression of the superconductivity.

Acknowledgements

The Academic Computer Center in Gdańsk (TASK), where all the calculations were performed, is acknowledged. Author profited from the fruitful discussions and especially close cooperation in the field of the computational techniques with Dr. R. Laskowski.

References


Charge distribution and magnetic interactions in \( PrBa_2Cu_3O_7 \)


This article was processed using the \LaTeX{} macro package with TTP style.
Electronic structure and charge distribution in DyBa$_2$Cu$_3$O$_7$: The ab initio approach

Maciej Łuszczek

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

A R T I C L E   I N F O

Article history:
Received 1 June 2009
Accepted 10 June 2009
Available online 14 June 2009

PACS:
74.72.-h
71.20.-b
71.15.Mb

Keywords:
Cuprate superconductors
Electronic structure
Density functional theory

A B S T R A C T

The full-potential linearized augmented plane wave (FP-LAPW) method was used for spin-polarized electronic structure calculations of stoichiometric DyBa$_2$Cu$_3$O$_7$ (Dy123) superconductor. The generalized gradient approximation plus Hubbard correction (GGA + U) was employed for Dy 4f electrons. The reference calculations of YBa$_2$Cu$_3$O$_7$ (Y123) were carried out in the spin-polarized mode to enable direct comparison. The determined total and atomic-projected densities of states (DOS), as well as charge distribution and on-site magnetic moments were analyzed and compared in detail. It was shown that in Dy123 system DOS in the close vicinity of the Fermi level is higher than in Y123. Also more efficient transfer of charge from CuO$_2$ planes was noticed in Dy123. The strongly localized magnetic spin moment of Dy is responsible for relatively weak magnetic interactions in the system, mostly in the CuO$_2$ planes. The obtained computational results are in agreement with the reported good superconducting properties of DyBa$_2$Cu$_3$O$_7$ compound.

1. Introduction

The correct understanding of electronic structure of RBa$_2$Cu$_3$O$_7$ (R=rare-earth) compounds upon rare-earth substitutions is still a challenge in the comprehension of the basic mechanism of superconductivity and its competition, coexistence and cooperation. Noteworthy, yttrium ions have also difficulty to incorporate into barium sites in the parent Y123 system, since the ionic radius of R ions is smaller than that of the light rare-earth ion (R = Nd, Sm, Eu, Gd), Therefore, these ions have also difficulty to incorporate into barium sites in the parent Y123 system for the same reason.

Since the discovery of high-temperature superconductivity in Y123, a large number of electronic structure calculations (mostly of the density-functional type) have been carried out as a first step in understanding the electronic properties of this material [8–10]. Soon, some members of R123 family of compounds have been examined by the ab-initio methods [11–18]. It was pointed out that all band structures are qualitatively similar. This is expected because the important Cu and O dominant bands should not be significantly affected by the substitution of Y with the trivalent rare-earth ion. One could suspect that the interaction of the 4f electrons of the rare-earth ions with the conduction electrons of the CuO$_2$ layers should be weak because of the spatial separation in the crystal lattice. It appears that some discrepancies in details of the band structure could be mainly a result of the different computational treatment of strongly localized R 4f states. It is also suggested that the on-site Coulomb repulsion of the 4f electrons should be accounted to improve the quality of calculations.

One can easily notice, however, that in the study of the R123 system main computational efforts have been concentrated on the explanation of the unusual insulating behavior of Pr123 compound and considerably less work has been done on the influence of the heavy (small) rare-earth ions on the electronic structure of the R123 system. Dy$^{3+}$ ion seems to be a good candidate for such investigation since, as was stated before, it (i) does not substitute for Ba atoms, (ii) could form well-defined orthorhombic, close to nominal, DyBa$_2$Cu$_3$O$_7$ phase and (iii) exhibits excellent superconducting properties, what enables the direct comparison with the Y123 compound.

In the present work the electronic band structure, charge distribution and magnetic interactions in stoichiometric DyBa$_2$Cu$_3$O$_7$ system have been determined by the spin-polarized full-potential...
linearized augmented plane wave (FP-LAPW) method and compared in detail with the YBa2Cu3O7 system.

2. Calculations

All calculations of DyBa2Cu3O7 were performed within the generalized gradient approximation (GGA) [19] using a local orbital extension (LO) of the full-potential linearized augmented plane wave (FP-LAPW) method [20]. The well-known WIEN2k code [21] was used for the band structure calculations. The crystallographic data collected in Ref. [22] were used as the input. Atomic sphere radii of 2 Å:

Dy

Ba, Cu, and O, respectively. Self-consistency was obtained using a set of 16 special k points in the irreducible Brillouin zone (IBZ).

The core and valence states were treated self-consistently, the former relativistically in an atomic-like approximation [23] and the later—scalar relativistically with spin–orbit interactions included in a second-variational procedure [24]. The starting (free-atom) electron configurations of the constituent atoms were as follows: Dy (Xe) 4f9 5d1 6s2, with seven spin-up (majority) and two spin-down (minority) 4f electrons; Ba (Xe) 6s2; Cu (Ar) 3d9 4s1; and O (He) 2s2 2p4. The GGA plus Hubbard parameter U (GGA + U) approach [25] was employed to account for the strong on-site Coulomb repulsion of the Dy 4f electrons. The U = 0.48 Ry and J = 0.078 Ry parameters were used (comparable with those applied for Pr 4f states in LSDA + U calculations of Pr123 [7]).

Although Y is non-magnetic, the reference GGA calculations of YBa2Cu3O7 were carried out in the spin-polarized mode to enable the direct comparison between the examined Dy123 and Y123 systems. The atomic sphere radii of Y and Ba were set to 2.3 Å and the initial electron configuration Y [Kr] 4d10 5s1 was used with the other parameters unchanged.

3. Results and discussion

The calculated energy bands of stoichiometric DyBa2Cu3O7 are typical for Y123 system (see Ref. [8] for the detailed description of bands in YBa2Cu3O7). Here the metallic character of the bands is visible, as well, with the dominant Cu(1) 3d–O(4) 2p (chain-derived) and Cu(2) 3d–O(2, 3) 2p (plane-derived) bands crossing the Fermi level. The high-lying empty bands have mostly Ba 4d character. One can also observe typical dispersion of E(k) in the x and y directions, indicating mainly two-dimensional behavior of carriers in the CuO2 planes and one-dimensional—in CuO chains.

The total densities of states (DOS) in DyBa2Cu3O7 and YBa2Cu3O7 systems are shown in Fig. 1. One can notice some additional narrow high-density peaks in Dy123 DOS (corresponding to Dy 4f–derived bands—see Fig. 3), when comparing with the Y123 system. Noteworthy, the GGA + U approach allows to overcome the observed shortcoming of GGA approximation, which puts the Dy 4f states at Fermi level (EF) and yields a fractional occupation, but not an atomic-like Dy3+ ion behavior. The implementation of U produces the Hubbard splitting between the occupied and empty 4f states and all Dy 4f minority spin states are entirely above the Fermi energy, whereas in the GGA approach these states were lying across the Fermi level producing significant splitting of spin states. As suspected, the band structure of Y123 does not exhibit noticeable splitting of “spin-up” and “spin-down” states in the full range of energy because of the non-magnetic character of yttrium ion.

It is worth to note at this place that spin-splitted band structure has been previously reported for large rare-earth R123 systems, namely, Ce123 (not synthesized as a single phase), Pr123 and Nd123 from LAPW–GGA calculations [17], where 4f states were treated as so-called “open cores”. In this technique 4f electrons of R were treated as strongly localized states, not hybridized with other valence electrons, and they were arbitrary shifted down in energy during the calculations to prevent their partial occupation at the Fermi level. In the present GGA + U approach the same effect is achieved but the splitting of spin states near EF is definitely smaller.

It is known that the energy gap 2Δ in the high-Tc copper oxide superconductors is roughly equal 50 meV [26], therefore it appears that the density of states in the nearest vicinity of the Fermi level

Fig. 1. Total density of states (DOS) of DyBa2Cu3O7 and YBa2Cu3O7 systems for the majority (up) and minority (down) spin states. The Fermi level was put at 0 eV.

Fig. 2. Details of total DOS of DyBa2Cu3O7 and YBa2Cu3O7 systems in the nearest vicinity of the Fermi level for the majority (up) and minority (down) spin states. The Fermi level was put at 0 eV.
should be very important in the context of superconductivity. The details of total DOS near \(E_F\) are shown in Fig. 2. As can be seen, there is no significant differences in shape between Dy123 and Y123 DOS curves at \(E_F\). The noticeable spin splitting of Dy123 bands (apparently followed by some magnetic interactions) occurs below the Fermi level, but it extends below \(-50\) meV and is not supposed to affect the superconductivity. On the other hand, Dy123 system exhibits slightly higher value of density of states at the Fermi level than Y123, that is, \(N_{\text{Dy123}}(E_F) = 3.16\) states/eV and \(N_{\text{Y123}}(E_F) = 3.04\) states/eV, what could imply even better superconducting properties of this compound.

Further detailed comparison of the studied systems is possible from partial (atomic) densities of states presented in Figs. 3 and 4. The analyzed band structures are essentially the same. As mentioned before, partial DOS of Dy in Dy123 is dominated by 4f peaks, whereas Y contribution to total DOS of Y123 is only marginal. In the both systems Ba atoms generate relatively small DOS in the valence bands and unoccupied states are shifted upwards by approximately \(3.5\) eV above \(E_F\). There are some noticeable differences between the partial DOS of Cu\((1)\) and Cu\((2)\). At a first glance, the spectral distributions are not quite the same: the plane Cu\((2)\) density of states at the Fermi level is significantly higher than that of Cu\((1)\).

**Fig. 3.** Partial DOS of DyBa\(_2\)Cu\(_3\)O\(_7\) system for the majority (up) and minority (down) spin states. The Fermi level was put at 0 eV.
Besides, although all the Cu bands extend to very similar positions at the top of the bands (2 eV), the chain-derived Cu(1) bands extend down only to (approximately) −5.5 eV, while the plane-derived Cu(2) bands extend to −7 eV. As could be seen from partial DOS curves, the plane O(2) and O(3) partial densities are practically identical, indicating that orthorhombicity arising from the chains has very little effect on the electronic structure of the CuO$_2$ planes. The plane O(2,3) valence bands extends from roughly −7 eV to 2 eV, that is, in the same range as Cu(2) bands. As the chain oxygens O(4) are considered, the partial DOS is lower than in the case of the O(2) and O(3) oxygens from the planes.

Interestingly, relatively high values of DOS are visible in the O(1) positions from the BaO layers. In the present calculations of Dy123 the total valence CuO bandwidth is 9 eV, whereas the CuO$_2$ chain bandwidth is 7.5 eV what is consistent with the previously reported partial DOS of R123 system for R = Y, Ce, Pr, Nd [8,13,17].

In the applied FP-LAPW method the electronic charge inside the unit cell is distributed either in the interstitial region or in the atomic spheres (giving so-called partial charges) where the symmetry decomposition according to $\mathbf{lm}$ can be made [10,21]. Partial charges (in electrons) corresponding to Dy(5s, 5p, 5d, 4f), Ba (6s, 5p, 5d), Cu(4s, 4p, 3d) and O(2s, 2p) majority and minority

![Fig. 4. Partial DOS of YBa$_2$Cu$_3$O$_7$ system for the majority (up) and minority (down) spin states. The Fermi level was put at 0 eV.](image_url)
spin valence states in DyBa₂Cu₃O₇ are collected in Table 1 and the symmetry decomposition of p and d states is presented in Table 2. Noteworthy, since the same radii were used for all copper and oxide spheres in the both systems, the direct comparison of partial charges at different Cu and O sites is also possible. One should be aware, however, that in the case of s and p states a large fraction of charge lies outside the atomic sphere.

As can be seen from Table 1, only small leakage of Dy 4f charge (0.07e) from the atomic sphere is visible, what means that f states are quite well spatially confined and therefore they cannot effectively hybridize with the other valence electrons. What is more, these states are strongly spin-polarized and thus responsible for magnetic interactions. The distribution of partial charges of Dy indicate almost nominal configuration 4f⁹ 5s⁵ 5p⁰ of isolated Dy⁺⁺⁺ ion with some fraction of charge shifted to d orbitals (0.36e). As shown in Table 2, pₓ, pᵧ, and pᶻ states of Dy are almost completely filled without significant anisotropy. The charges of dₓz, dᵧz, and dₓ²−y² symmetries are smaller than that of the dₓz−y², dₓ² and dₓz. Some part of the valence charge is lost by Ba atoms, as well. One can also notice that Cu charges are dominated by dₓz−y² component. For both copper sites, the highest partial charges correspond to dₓz, dₓ², and dₓz−y² orbitals, which are nearly filled, what means that the interactions with neighbors are weak. On the contrary, the Cu(1) atoms from chains gather the smallest charge in the dₓz and dₓ²−y² symmetries, respectively, as a result of strong interactions with p orbitals of O(1) and O(4). On the other hand, the Cu(2) atoms in the planes have less charge in the dₓz−y² state than in dₓz due to strong interactions with the O(2) and O(3) atoms. Similar analysis can be performed for oxygen p states. The O(2) sphere is involved in strong interaction mainly in x direction (parallel to the a axis of the unit cell), thus the pₓ partial charge is the smallest. An analogous situation occurs for the O(3) position, but interactions have mostly y (parallel to b axis) character with the smallest value of pᵧ charge. Consequently, the strongest interactions can be determined along the c axis for O(1) atom, what is indicated by the smallest value of the partial charge with the pᵧ symmetry, and, finally, for O(4)—along the chains (the smallest pₓ component).

The same picture of interactions arises from the analysis of partial charges in YBa₂Cu₃O₇ system, as can be seen from Tables 3 and 4, and is consistent with the reported results of local-density approximation (LDA) calculations in non-spin-polarized study of Y123 [10]. In the present GGA approach the most significant differences appear in Y(3s, 5p 4d) and Ba(6s, 5p 5d) partial charges, when compared with Dy123, mainly as a result of lack of 4f electrons in Y. Besides, one should also remember that Y and Ba have slightly larger atomic spheres in the calculations of Y123 (see computational details in Section 2), what could also influence the corresponding partial charges. In the both systems the Cu(2)

---

**Table 1**

Partial charges corresponding to the majority and minority spin valence states in DyBa₂Cu₃O₇ system. All data is given in electrons (e).

<table>
<thead>
<tr>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
<th>Total</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>0.9976</td>
<td>2.7509</td>
<td>0.1916</td>
<td>6.9004</td>
<td>10.8432</td>
</tr>
<tr>
<td>Ba</td>
<td>1.0078</td>
<td>2.8438</td>
<td>0.2224</td>
<td>0.0194</td>
<td>4.0992</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0.9178</td>
<td>3.0914</td>
<td>0.4979</td>
<td>0.0111</td>
<td>7.5209</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.9180</td>
<td>3.0756</td>
<td>0.4392</td>
<td>0.0085</td>
<td>7.5162</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.7736</td>
<td>1.6951</td>
<td>0.0044</td>
<td>0.0008</td>
<td>2.4749</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.7714</td>
<td>1.7118</td>
<td>0.0053</td>
<td>0.0009</td>
<td>2.4889</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.7720</td>
<td>1.7117</td>
<td>0.0050</td>
<td>0.0008</td>
<td>2.4898</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.7743</td>
<td>1.6788</td>
<td>0.0041</td>
<td>0.0008</td>
<td>2.4582</td>
</tr>
</tbody>
</table>

---

**Table 2**

Symmetry decomposition of p and d majority and minority valence states in DyBa₂Cu₃O₇. All data is given in electrons (e).

<table>
<thead>
<tr>
<th>dₓz−y²</th>
<th>dₓ²</th>
<th>dₓz</th>
<th>pₓ</th>
<th>pᵧ</th>
<th>pᶻ</th>
<th>pₓ²−y²</th>
<th>pₓ²</th>
<th>dₓz−y²</th>
<th>dₓ²</th>
<th>dₓz</th>
<th>pₓ²−y²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>0.9712</td>
<td>0.9155</td>
<td>0.9183</td>
<td>0.0185</td>
<td>0.0509</td>
<td>0.0165</td>
<td>0.0553</td>
<td>0.0511</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.9709</td>
<td>0.9065</td>
<td>0.9090</td>
<td>0.0163</td>
<td>0.0453</td>
<td>0.0145</td>
<td>0.0488</td>
<td>0.0449</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(1)</td>
<td>1.0109</td>
<td>1.0318</td>
<td>1.0487</td>
<td>0.6932</td>
<td>0.8236</td>
<td>0.9228</td>
<td>0.9247</td>
<td>0.9335</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(2)</td>
<td>1.0251</td>
<td>1.0304</td>
<td>1.0127</td>
<td>0.8782</td>
<td>0.7053</td>
<td>0.9271</td>
<td>0.9099</td>
<td>0.9090</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>0.9500</td>
<td>0.6064</td>
<td>0.4987</td>
<td>0.0016</td>
<td>0.0001</td>
<td>0.0004</td>
<td>0.0009</td>
<td>0.0008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>0.9500</td>
<td>0.6066</td>
<td>0.4988</td>
<td>0.0016</td>
<td>0.0001</td>
<td>0.0004</td>
<td>0.0009</td>
<td>0.0008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>0.9500</td>
<td>0.6063</td>
<td>0.4979</td>
<td>0.0016</td>
<td>0.0001</td>
<td>0.0004</td>
<td>0.0009</td>
<td>0.0008</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Table 3**

Partial charges corresponding to the majority and minority spin valence states in YBa₂Cu₃O₇ system. All data is given in electrons (e).

<table>
<thead>
<tr>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
<th>Total</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>0.7739</td>
<td>1.6999</td>
<td>0.0043</td>
<td>0.0008</td>
<td>2.4798</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.7722</td>
<td>1.7191</td>
<td>0.0053</td>
<td>0.0010</td>
<td>2.4696</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.7718</td>
<td>1.7175</td>
<td>0.0050</td>
<td>0.0008</td>
<td>2.4584</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.7742</td>
<td>1.6850</td>
<td>0.0042</td>
<td>0.0008</td>
<td>2.4645</td>
</tr>
</tbody>
</table>

---

**Table 4**

Symmetry decomposition of p and d majority and minority valence states in YBa₂Cu₃O₇. All data is given in electrons (e).

<table>
<thead>
<tr>
<th>dₓz−y²</th>
<th>dₓ²</th>
<th>dₓz</th>
<th>pₓ</th>
<th>pᵧ</th>
<th>pᶻ</th>
<th>pₓ²−y²</th>
<th>pₓ²</th>
<th>dₓz−y²</th>
<th>dₓ²</th>
<th>dₓz</th>
<th>pₓ²−y²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>0.9483</td>
<td>0.9465</td>
<td>0.9488</td>
<td>0.0213</td>
<td>0.0601</td>
<td>0.0193</td>
<td>0.0647</td>
<td>0.0589</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.9483</td>
<td>0.9465</td>
<td>0.9488</td>
<td>0.0213</td>
<td>0.0601</td>
<td>0.0193</td>
<td>0.0647</td>
<td>0.0589</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(1)</td>
<td>1.0109</td>
<td>1.0318</td>
<td>1.0479</td>
<td>0.6960</td>
<td>0.8243</td>
<td>0.9236</td>
<td>0.9255</td>
<td>0.9350</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(2)</td>
<td>1.0334</td>
<td>1.0305</td>
<td>1.0127</td>
<td>0.8788</td>
<td>0.7424</td>
<td>0.9293</td>
<td>0.9118</td>
<td>0.9112</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
atomic spheres contain less charge than the Cu(1) spheres (see Tables 1 and 3), indicating some transfer of electrons from CuO planes to CuO chains. In Dy123 system this effect seems to be even a little bit stronger than in Y123. Moreover, the summarized charge in CuO planes in Dy123 is less by about 0.04 electrons than in analogous planes in Y123 system. Noteworthy, many authors believe that conduction occurs mainly in the CuO planes while the CuO chains act as “charge reservoirs”, which provide carriers (holes) to the CuO planes. Within this concept, one can hypothesize that the enlarged hole concentration in planes could coincide with some improvement of superconducting properties.

As can be also noticed from Tables 1 and 2, some differences in values of partial charges corresponding to the majority and minority spin states are visible. Certainly, in the Dy atomic sphere the disproportion between “spin-up” and “spin-down” charges is the largest because of the presence of 4f electrons. The copper and oxide spheres are less affected. The noticeable differences between the majority and minority partial charges occur in the Cu(2) spheres for the \( \Delta \rho_{x} \) and \( \Delta \rho_{y} \) symmetries, indicating some in-plane magnetic interactions. The slightly weaker polarization of charges at the Cu(1) site has mostly \( \Delta \rho_{z} \) character, apparently due to relatively strong interaction with O(1). The small difference in charge amount for the both spins in the atomic spheres of plane O(2) and O(3) oxygens could result from weak “connection” between planes and chains in the orthorhombic crystal structure. In the Y123 system spin polarization of partial charges is definitely weaker (see Tables 3 and 4), as suspected. Interestingly, small disproportion in d-type majority and minority charges appears only in the Cu(1) atomic spheres from the chains.

The above-mentioned differences in the partial charges corresponding to the majority and minority spins are, naturally, followed by the appearance of the on-site magnetic spin moments. The values of z-axis – projected spin moments \( \mu_{z} \) in DyBa\(_{2}\)CuO\(_{4}\) and YBa\(_{2}\)CuO\(_{4}\) are listed in Table 5. It is clear that in the Dy123 system the values of magnetic moments are generally higher than in Y123. The strong localized magnetic moment \( \mu_{z}(\text{Dy}) = 4.92 \mu_{B} \) is visible, which is responsible for the generation of magnetic interactions in the CuO planes with \( \mu_{z}(\text{Cu}(2)) = 0.021 \mu_{B} \). Interestingly, \( \mu_{z}(\text{Cu}(2)) \) is approximately twenty times larger than that of O(3). For the O(1) and O(4) sites, in turn, the determined values of spin moments are identical and higher than \( \mu_{z}(\text{Cu}(1)) \). In contrary to the Dy123 system, in Y123 the only significant magnetic interactions occur predominantly in the CuO chains but still \( \mu_{z}(\text{Cu}(1)) \) is lower than that induced in the O(4) sphere. It is worth to note that in this case \( \mu_{z}(\text{O}(4)) \) is about four times larger than \( \mu_{z}(\text{O}(1)) \).

### Table 5

<table>
<thead>
<tr>
<th></th>
<th>( \mu_{z} ) (in ( \mu_{B} )) inside atomic spheres in DyBa(<em>{2})CuO(</em>{4}) and YBa(<em>{2})CuO(</em>{4}) systems.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>Y</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0.00025</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.00020</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.00045</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.00012</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.00066</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.00045</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In the present work the full-potential linearized augmented plane wave (FP-LAPW) method has been used for the spin-polarized electronic structure calculations of stoichiometric DyBa\(_{2}\)CuO\(_{4}\) (Dy123) superconductor. The generalized gradient approximation plus Hubbard correction (GGA + U) was employed for Dy 4f electrons to prevented fractional occupation of states at the Fermi level and hybridization with other valence electrons. The reference calculations of YBa\(_{2}\)CuO\(_{4}\) (Y123) have been carried out in the spin-polarized mode, to enable direct comparison between the both studied systems. The electronic structure of Dy123 is generally consistent with the previous calculations of the Y123-like systems. The higher value of density of states (DOS) near the Fermi level and more efficient transfer of charge from the CuO planes (increased hole concentration) were determined for the Dy123 system when compared with the parent Y123. The strongly localized magnetic spin moment of Dy introduces relatively weak magnetic interactions to the system, mostly into CuO planes.

To conclude, the presented results indicate very good potential superconducting properties of the DyBa\(_{2}\)CuO\(_{4}\) material what is in agreement with the experiment.

### Acknowledgement

The Academic Computer Center in Gdańsk (TASK), where all the calculations were performed, is acknowledged.

### References

Electronic structure of TbBa$_2$Cu$_3$O$_7$

Maciej Łuszczek*

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

Received 4 May 2009, revised 28 June 2009, accepted 2 July 2009

Published online 29 October 2009

PACS 71.15.Mb, 71.20–b, 74.72–h

*Corresponding author: e-mail maclu@mif.pg.gda.pl, Phone: +4858 3471310, Fax: +4858 3472821

1 Introduction

RBa$_2$Cu$_3$O$_7$ (R = rare earth) denoted as R123 hereafter was the first series of compounds for which it was discovered that a diamagnetic ion Y could be replaced by a magnetic rare earth without influencing the high $T_C$ superconducting properties [1]. It was also noted that there were three R ions that could not be substituted to produce a superconductor, namely, Ce, Pr and Tb. Moreover, it was suspected that these three ions could be in stable tetravalent state in the R123 system. However, a wide range of data on R = Pr analogue strongly suggest that the ‘hole-filling’ mechanism due to +4 valency of Pr is incorrect [2, 3] since this ion appears to be essentially trivalent. Some other models, such as e.g. magnetic pair breaking, carrier localization, Pr$_{4f–O2p}$ hybridization, have been proposed to explain the intriguing suppression of superconductivity in Pr123. The $ab$ $initio$ electronic structure calculations of PrBa$_2$Cu$_3$O$_7$ were carried out as a first step in understanding the electronic properties of these materials [4–7]. It was shown that electronic bands have metallic character like in the parent superconducting YBa$_2$Cu$_3$O$_7$ system. The discovery of superconductivity in Pr123 [8–12] made the situation even more complicated. There is a strong experimental evidence that some fraction of Ba sites in the R123 lattice is occupied by the rare-earth ions. In this picture, the magnetic Ce$^{3+}$ and Tb$^{3+}$ are unique because of their large size which allows them to occupy the Ba sites without the significant lattice distortion. Therefore, it has been argued that Pr at the Ba site (Pr$_{Ba}$), and not the R site, destroys the superconductivity by the large magnetic moment of Pr$^{3+}$ since the superconducting carriers were first proposed to occupy the vicinity of the chains [13] and more recently have been located in the BaO layers [14]. To find out if Pr at the Ba site could significantly influence the electronic structure of Pr123 system the self-consistent calculations were performed [15]. As a first approach the Pr$_{Ba}$ defect was simulated by simple exchanging of Pr and one of Ba atoms in the unit cell. It was shown that Pr-Ba disorder affects the electronic band structure. Interestingly, some spin splitting in the density of states (DOS) was observed mostly for chain-derived states. It was hypothesized that, as a consequence, some effective magnetic moment, located predominantly in the chain layers, could be generated. As a next step, the 54-atom supercell model of PrBa$_2$Cu$_3$O$_7$ with one Pr$_{Ba}$ defect and the additional anti-chain O(5) oxygen has been examined by the first-principles method [16]. It appears from the cited calculations that some redistribution of total charge in both the CuO planes and chains takes place whereas the charges of barium and oxygen in the BaO layer remain unchanged when comparing with the stoichiometric Pr123 system. It has been also shown that Pr$_{Ba}$ defect produces localized magnetic moment in the BaO layer and additionally enhanced magnetic moments are induced on the

The full-potential linearized augmented plane wave (FP-LAPW) method was used for spin-polarized electronic structure calculations of stoichiometric TbBa$_2$Cu$_3$O$_7$ (Tb123), not synthesized as a single phase yet. The generalized gradient approximation plus Hubbard correction (GGA + $U$) was employed for Tb$4f$ electrons to prevented fractional occupation of states at Fermi level and hybridization with other electrons. The determined band structure is Y123-like with the metallic character as in the other superconducting R123 (R = rare earth). The presented results indicate that strong on-site spin moment of Tb could not effectively influence the neighbours and the induced magnetic interactions in the system are weak (CuO planes) or negligible (BaO planes and CuO chains). This appears to be the repercussion of the ‘size effect’ due to relatively small Tb$^{3+}$ ionic radius. The predicted weak influence of magnetic moments of Tb on CuO states in the assumed (hypothetical) Fermi liquid phase of TbBa$_2$Cu$_3$O$_7$ could favour the rise of superconductivity in this system.
Cu(2) sites in the CuO planes. In contrary to previous calculations, the magnetic moments of Cu(1) in the chains remain practically unaffected.

There has been considerably less work done on the roles of Ce and Tb in suppressing $T_C$. At least in part, this is because Ce and Tb do not form single ‘123’ phase. For the case of Tb123, obtaining the phase has not been possible with the composition TbBa$_2$Cu$_3$O$_7$ by any means due to strong intermixing of Tb and Ba at their respective sites [17, 18]. However, a comparative study of partially substituted thin film Y123 samples revealed that Tb does not behave in the same manner as Ce or Pr [19] when it is incorporated into a superconducting phase. It was shown that the partial substitution of Pr or Ce have detrimental effects on sample conductivity and superconductivity, whereas Tb was found to substitute for Y without significant effects on either the normal state conductivity or $T_C$. On the other hand, Ce and Pr both increase resistivity in the normal state and monotonically decrease superconducting critical temperature. What is more, the recent study of Tb oxidation state [20] has confirmed the existence of Tb$^{+3}$ in this system. It has been argued that this essential difference could be explained by the R$_A$ disorder, as well, because Tb, contrary to Ce and Pr, should have difficulty occupying Ba site in R123 being to small to efficiently bond to the nearest neighbours [21].

The purpose of the present work is to study the band structure of TbBa$_2$Cu$_3$O$_7$, which is the next after Ce123 not synthesized as a single phase ‘intriguing’ R123 compound. We also want to compare the electronic structure of Tb123 with the previously performed calculations of Pr123 and Ce123 systems [16, 22].

2 Computational details Present calculations were performed within the generalized gradient approximation (GGA) [23] using a local orbital extension (LO) of the full-potential linearized augmented-plane wave (FP-LAPW) method [24, 25]. The well-known WIEN2k code [26, 27] was used for the band structure calculations. Atomic sphere radii of 2.20, 2.20, 1.90 and 1.55 a.u. were taken for Tb, Ba, Cu and O, respectively. Self-consistency was obtained using a set of 16 special $k$ points in the irreducible Brillouin zone (IBZ). The core and valence states were treated self-consistently, the former relativistically in an atomic-like approximation [28] and the later – scalar relativistically with spin-orbit interactions included in a second-variational procedure [29]. The starting electron configuration for Tb was [Xe] 4f$^8$ 5d$^1$ 6s$^2$ with 7 spin-up (majority) and 1 spin-down (minority) 4f electrons. The GGA plus Hubbard parameter $U$ (GGA + $U$) approach [30] was employed to account for the strong on-site Coulomb repulsion of the Tb4f electrons. The $U$ and $J$ parameters were set to 0.40 and 0.07 Ry, respectively, very close to values reported for LSDA + $U$ calculations of Pr123 [7].

As mentioned before, single-phase TbBa$_2$Cu$_3$O$_7$ has not been synthesized yet and thus the hypothetical crystal structure had to be assumed. As a first step, we chose the lattice parameters comparable with those reported for GdBa$_2$Cu$_3$O$_7$ from the low-temperature neutron-diffraction study [31] since Tb$^{+3}$ and Gd$^{+3}$ have similar ionic radii.
3 Results and discussion

The energy bands of stoichiometric TbBa$_2$Cu$_3$O$_7$ obtained from GGA + $U$ calculations are presented in Fig. 1. At a first glance, the band structure is Y123-like and generally consistent with the previous calculations of R123 with R = Y, Ce, Pr and Nd [22]. The metallic character of the system is visible with the dominant Cu(1)3$d$–O(4)2$p$ chain- and Cu(2)3$d$–O(2,3)2$p$ plane-related bands crossing the Fermi level. The high-lying empty bands have mostly Ba4$d$ character. One can also notice typical dispersion of $E(k)$ in the $x$ and $y$ directions responsible for two-dimensional character of the bands. Therefore, it could be merely pointed out that all R123 band structures are almost the same. This is expected because the important Cu and O dominant bands should not be significantly affected by the substitution of Y with the trivalent rare earth [4].

Noteworthy, the GGA + $U$ approach allows to overcome the observed shortcoming of GGA approximation, which puts the Tb4$f$ states at Fermi level and yields a fractional occupation, but not an atomic-like Tb$^{3+}$ ion behaviour. The
implementation of $U$ produces the Hubbard splitting between the occupied and empty $4f$ states. In the GGA + $U$ calculations Tb$4f$-minority spin states are entirely above the Fermi energy, whereas in the GGA approach these states lie across the Fermi level producing significant spin splitting. The comparison of band structure in the both cases is possible from the total density of states (DOS) plots presented in Fig. 3. One can easily notice the narrow Tb$4f$-derived band at $E_F$, which is responsible for the spin splitting in the GGA calculations (Fig. 2a). On the other hand, the applied $U$ Hubbard parameter causes the shift of the $4f$ spin states resulting in suppression of the splitting near the Fermi level (Fig. 2b).

It is worth to note at this place that spin-splitted band structure has been previously reported either for Pr$123$ or Ce$123$ (not synthesized as a single phase) from LAPW-GGA calculations [22] where $4f$ states were treated as the so-called ‘open cores’, that is, they were arbitrary shifted down in energy during the calculations to prevent their partial occupation at Fermi level. In this technique, $4f$ electrons of R atoms are treated as strongly localized states and their hybridization with the other valence electrons should be negligible. In present GGA + $U$ approach the same effect is achieved. This, in turn, is consistent with the experimental data indicating that Tb ion states are not hybridized [20].

One more remark concerning the GGA + $U$ approach should be added here. It is well known that including or excluding Hubbard correction for Cu $d$ states may discriminate between the Mott insulating and the Fermi metal phase. However, $U$ is the external parameter and in general different values for different Cu sites should be tested to ‘calibrate’ the method according to the experimental data, which in the case of Tb$123$ is insufficient. Hence, at present stage of investigation this correction for Cu was not applied.

The electronic band structure of Tb$123$ from GGA + $U$ calculations could be studied in detail from the projected (atomic) DOS characteristics, which are shown in Fig. 3. As it was stated before, Tb$4f$-spin-up and spin-down peaks are shifted due to $U$ correction and thus removed from $E_F$. The highest density of occupied terbium majority spin states is visible at about $-5$ eV. One can also notice relatively low DOS of Ba valence bands. The highest contributions to total DOS come from Cu(1) and Cu(2) sites. As oxygen atoms are concerned, the highest DOS is observed for O(1) from BaO layer. The DOS values for CuO-plane O(2) and O(3) atoms are similar. The lowest density of states is connected with the chain O(4) site.

The values of DOS at Fermi level $D(E_F)$ and on-site spin magnetic moments calculated for all atoms are collected in Table 1. The highest $D(E_F)$ has been determined for Cu(2) from CuO planes, whereas the contributions from Ba and Tb are negligible. One could also immediately notice that the strongly localized magnetic spin moment of Tb (approximately $5.92 \mu_B$) induces weak magnetic spin moments in Cu(2)–O(2,3) planes, while magnetic interactions in Ba–O(1) planes and Cu(1)–O(4) chains could be essentially neglected.

### Table 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>$D(E_F)$ (states/eV)</th>
<th>Magnetic spin moment ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>0.041</td>
<td>5.91645</td>
</tr>
<tr>
<td>Ba</td>
<td>0.015</td>
<td>0.00012</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0.295</td>
<td>0.00013</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>1.090</td>
<td>$-0.00220$</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.424</td>
<td>$-0.00006$</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.305</td>
<td>$-0.00466$</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.313</td>
<td>$-0.00113$</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.230</td>
<td>0.00001</td>
</tr>
<tr>
<td>total</td>
<td>3.217</td>
<td>5.96838*</td>
</tr>
</tbody>
</table>

The size of the corresponding atomic sphere is given in ‘Computational details’.

Interestingly, although Tb exhibits almost 4 times stronger spin moment than that calculated for Pr in the stoichiometric PrBa$_2$Cu$_3$O$_7$ ($\mu_B \cong 1.5 \mu_B$) [16], the CuO chains and planes in Tb$123$ are definitely less affected. The analogous Cu(1) and Cu(2) spin moments in perfect Pr$123$, obtained from GGA calculations, were equal $-0.010$ and $-0.037 \mu_B$, respectively. This is probably the repercussion of the ‘size effect’ since Tb$^{3+}$ has significantly smaller ionic radius than Pr$^{3+}$ or Ce$^{3+}$ and it is not able to effectively influence the neighbours.

### 4 Summary and conclusions

Electronic structure of stoichiometric TbBa$_2$Cu$_3$O$_7$ (not synthesized as a single phase yet) was calculated using FP-LAPW method. The GGA + $U$ approach was employed for Tb$4f$ states to account for the strong on-site Coulomb repulsion. It was shown that obtained band structure is Y123-like and qualitatively similar to RBa$_2$Cu$_3$O$_7$ with R = Ce, Pr, Nd and Gd reported from the previous self-consistent ab initio calculations [4–7, 15, 16, 22]. It appears that some discrepancies in details of the band structure could be mainly a result of the different computational treatment of strongly localized $4f$ states. In the case of Tb$4f$ electrons, Hubbard correction seems to be a good choice because it allows to prevent the fractional occupation at Fermi level and the hybridization with the other electrons. This approach is consistent with the experimental data indicating that Tb ion states are not hybridized [20].

The presented results show that strong on-site spin moment of Tb could not effectively influence the neighbours. Therefore, the induced magnetic interactions in the Cu(2)–O(2,3) planes are weak and in Ba–O(1) planes or in Cu(1)–O(4) chains are essentially negligible. This is apparently the repercussion of the ‘size effect’ due to relatively small Tb$^{3+}$ ionic radius.

To conclude, the predicted weak influence of magnetic moments of Tb on CuO states in the assumed (hypothetical) Fermi liquid phase of TbBa$_2$Cu$_3$O$_7$ could favour the rise of superconductivity in this system.
Acknowledgements The Academic Computer Center in Gdańsk (TASK), where all the calculations were performed, is acknowledged.

References

Electronic structure of PrBa$_2$Cu$_3$O$_7$ after high-pressure compression from first principles

Maciej Łuszczek

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

A R T I C L E   I N F O

Article history:
Received 9 June 2010
Accepted 19 October 2010
Available online 28 October 2010

Keywords:
Cuprate superconductors
Electronic structure
Density functional theory

A B S T R A C T

The influence of the high-pressure compression ($P \approx 9$ GPa) on the electronic band structure, charge distribution and magnetic moments of the fully oxygenated, ideally stoichiometric PrBa$_2$Cu$_3$O$_7$ system was investigated. The following changes were observed as a result of the simulated compression: (i) the reduced total density of states (DOS) at the Fermi level $E_F$, (ii) the increased difference between spin-up and spin-down total DOS in the nearest vicinity of $E_F$ (spin splitting), (iii) the lowered occupation of Pr 4f band crossing $E_F$, (iv) the stronger localization of partial charges in all atomic spheres, (v) the reduced amount of holes in the CuO$_2$ planes and (vi) the enhanced magnetic moments in the system, especially in the cupric-oxide planes. Our results indicate the possibility of negative pressure effect on the superconductivity in the optimally doped PrBa$_2$Cu$_3$O$_7$ system at the sufficiently high hydrostatic pressure.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

PrBa$_2$Cu$_3$O$_{7-x}(P123)$ compound is perhaps the most extensively investigated member of the (rare-earth) Ba$_2$Cu$_3$O$_{7-x}$ family of high-$T_c$ superconductors because of its specific structural and transport properties. It is isostructural to the other superconducting rare-earth homologues but it exhibits neither metallic nor superconducting properties on the macroscopic scale and a reduced total density of states (DOS) at the Fermi level $E_F$.

It was demonstrated, however, that Pr123 could be a superconductor [6–11]. The synthesis of superconducting PrBa$_2$Cu$_3$O$_7$ crystals with $T_c = 85$ K by the use of the traveling-solvent floating-zone (TSFZ) method was successfully performed [9,10] and soon the positive pressure effect on $T_c$ was observed [12]. Interestingly, the high oxygen deficiency gave higher $T_c$ enhancement. The maximum value of the onset and the zero-resistance $T_c$ under pressure in initially undoped crystals ($x = 6.6$) was above 105 K at 9.3 GPa. In accordance with an increase in the applied hydrostatic pressure, the unit cell volume showed a monotonical decrease reaching approximately 94% of its initial value and no trace of structural transition was recognized.

The pressure dependence of critical temperature $T_c(P)$ in the discovered superconducting Pr123 crystals is quite well reproduced by the $t$-$t'$-$J$ model [13] arriving at the conclusion that the unusually large $T_c$ enhancement in this compound results from its underdoped nature. The $T_c$ in PrBa$_2$Cu$_3$O$_x$ compound, with assumed $T_c = 85$ K (underdoped system) in ambient pressure, as a function of pressure $P$ in the range of $0 \leq P \leq 20$ GPa was calculated giving as a result a parabolic-shaped curve with the maximum of 105.6 K at 9.7 GPa in very good agreement with the experiment [12]. The value of $T_c$ is reaching 95 K at 3.2 GPa, the predicted maximum value of $T_c$ at ambient pressure. Noteworthy, the predicted $T_c$ at $P = 20$ GPa is also equal 95 K, hence, it is still enhanced when compared with the initial ambient-pressure value of 85 K. On the other hand, the theoretically evaluated $T_c(P)$ in the range of $0 \leq P \leq 10$ GPa for the optimally doped Pr123 with initial $T_c = 95$ K passes through a maximum of 97.2 K at $P = 4$ GPa and then rapidly decreases to reach about 90 K at $P = 10$ GPa. Thus, the negative pressure effect is predicted for the fully oxygenated PrBa$_2$Cu$_3$O$_7$ compound under the high-pressure compression $P > 4$ GPa. Interestingly, structural and electronic properties of the parent YBa$_2$Cu$_3$O$_7$ compound calculated by the use of the ab initio total energy-pseudopotential method indicate positive pressure effect in the full range of $0 \leq P \leq 12$ GPa [14].

As described above, two main situations for Pr123 in the range $9 \leq P \leq 10$ GPa could potentially take place, namely, (i) the maximal increase of the initial $T_c$ for the underdoped system and (ii) the significant decrease of the initial $T_c$ for the optimally doped system [13]. The aim of this work is to study the electronic structure, charge distribution and magnetic moments obtained from the first principles calculations of fully oxygenated, ideally stoichiometric PrBa$_2$Cu$_3$O$_7$ system to find out if the negative pressure effect is plausible in this compound under the high-pressure compression of $P \approx 9$ GPa.
2. Calculations

Present calculations of Pr123 in ambient pressure were performed using available crystallographic data: $a = 3.8588 \, \text{Å}$, $b = 3.9275 \, \text{Å}$, $c = 11.7106 \, \text{Å}$ [15]. We simulated the high-pressure compression $P \approx 9 \, \text{GPa}$ by the appropriate shortening of the lattice constants ($a = 3.7816 \, \text{Å}$, $b = 3.8489 \, \text{Å}$, $c = 11.4764 \, \text{Å}$) to achieve reduction of the initial unit cell volume comparable with the reported for such pressure from the experiment (i.e. the compression to about 94% of the initial volume) [12] with the fixed relative positions of atoms. It seems to be a reasonable choice, because, as it was previously shown from the ab initio calculations of pressure effect in YBa2Cu3O7, in the first approximation, all atomic coordinates should scale with the lattice parameters [14].

We have performed the self-consistent spin-polarized electronic structure calculations within density functional theory (DFT) [16] using generalized gradient approximation (GGA) [17] and a local orbital (LO) extension of full-potential linearized augmented plane wave (FP-LAPW) method [18]. In this method the Kohn–Sham orbitals [19] are expanded in atomic-like orbitals in the muffin-tin spheres and plane waves in the interstitial region. The basis set inside each MT sphere is split into core and valence subsets. The core states are treated within the spherical part of the potential and are assumed to have a spherically symmetric charge density totally confined inside the muffin-tin spheres. The valence part is treated within a potential expanded into spherical harmonics. In our calculations the core and valence states were treated self-consistently, the former relativistically in an atomic-like approximation [20] and the latter—scalar relativistically with spin–orbit interactions included in a second-variational procedure [21].

The details of the initial electron configurations taken for our calculations are collected in Table 1. The MT radii of 2.3 bohr were used for both Pr and Ba, whereas 1.9 bohr and 1.55 bohr were applied for Cu and O, respectively. In the presented approach the basis set of 1221 plane waves and 107 local orbitals was applied and the plane-wave cutoff $R_{\text{min}}K_{\text{max}} = 6.0$ was chosen, where $R_{\text{min}}$ denotes the smallest atomic sphere radius and $K_{\text{max}}$ gives the magnitude of the largest $K$ vector in the plane-wave expansion. Self-consistency was obtained using a set of 16 special $k$ points in the irreducible Brillouin zone (IBZ) with the charge density taken as a criteria of convergence (the “charge distance” of the order of $10^{-5}$ e between the successive iterations was reached). The GGA plus Hubbard parameter $U_{\text{Pr}}$ (GGA+$U$) approach [22] was employed to account for the strong on-site Coulomb repulsion of the Pr 4f electrons with $U_{\text{Pr}} = 0.4 \, \text{Ry}$ and $J_{\text{Pr}} = 0.07 \, \text{Ry}$ parameters (comparable with those applied for Pr 4f states in reported LSDA+$U$ calculations of Pr123 [23]). One should remember, however, that $U_{\text{Pr}}$ is the external parameter and in general different values could be tested to “calibrate” the method according to the experimental data (see Ref. [23] for the discussion), which in the case of the compressed Pr123 system is insufficient. Hence, at the present stage of the investigation this parameter was chosen arbitrary. It was reported in the literature that GGA can quite properly reproduce many physical properties of the metallic (doped) high-$T_c$ superconductors without application of Hubbard correction for Cu 3d states but, on the other hand, $U_{\text{Cu}}$ parameter could play the crucial role in the case of the underdoped materials [24]. It is also well known that including or excluding $U_{\text{Cu}}$ for Cu 3d states may discriminate between the Mott insulating and the Fermi metal phase. In other words, with such a choice of $U_{\text{Cu}}$ the fact that band energy corresponds to the latter case is in some sense predetermined. Furthermore, one should be aware that $U_{\text{Cu}}$ is another external parameter and in general different values for different Cu sites in Pr123 could be considered [23] what makes the analysis even more complicated. In this comparative study we assumed the optimally doped (metallic) character of the Pr123 system and thus this correction for Cu 3d states was not applied.

### Table 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>Configuration</th>
<th>Core states</th>
<th>Valence states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>[Xe] 4f^5d^6s^2</td>
<td>[Kr] 4f^10</td>
<td>4f^5s^5g^5d^6s^2</td>
</tr>
<tr>
<td>Ba</td>
<td>[Xe] 6s^2</td>
<td>[Kr] 4f^10</td>
<td>5f^2g^2s^2</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar] 3d^4s^2</td>
<td>[Ne] 3s^2</td>
<td>3p^3s^d^4s^2</td>
</tr>
<tr>
<td>O</td>
<td>[He] 2s^2p^4</td>
<td>[He]</td>
<td>2s^2p^4</td>
</tr>
</tbody>
</table>

Fig. 1. Total density of states (DOS) of PrBa2Cu3O7 in ambient pressure (upper) and after the high-pressure compression (lower) for the majority (up) and minority (down) spin states. The Fermi level was put at 0 eV.
comparable critical temperatures of the compressed Pr123 and Dy123 (or Y123) in the ambient pressure environment.

It is commonly accepted that the density of states in the nearest vicinity of the Fermi level seems to be a very important parameter in the context of the superconductivity (the energy gap in the high-$T_c$ copper oxide superconductors is roughly 50 meV [28]). The details of total DOS near $E_F$ are shown in Fig. 2. One can suspect that the visible enhanced spin splitting of Pr123 bands after the compression, that is, the difference between ‘spin-up’ and ‘spin-down’ DOS which occurs around the Fermi level, could affect the superconductivity. The determined differences in spin-polarized DOS at $E_F$ are equal approximately $\Delta N(E_F) = 0.10$ states/eV and $\Delta N(E_F) = 0.32$ states/eV for uncompressed and compressed systems, respectively. At the $E = -50$ meV the spin splitting is definitely stronger: $\Delta N(E) = 2.06$ states/eV under the high pressure and $\Delta N(E) = -0.86$ states/eV in the ambient pressure (note the change in the sign).

It was proposed in the literature that hole localization due to strong hybridization between Pr 4f and O 2p orbitals could be responsible for the suppression of superconductivity in the conventional Pr123 compound [29–31]. If we assume that the application of pressure decreases the distances between Pr and the nearest O atoms, the hybridization might be expected to increase after the strong compression. This increasing hybridization may, as a consequence, lead to stronger localization of carriers and result in the negative pressure effect. Indeed, our calculations show, to some extent, that this situation is plausible. As could be seen from Fig. 3, the Pr 4f majority states (‘spin-up’) are shifted upwards and therefore become less occupied (what means more holes). As a result, density of Pr 4f states at $E_F$ increases from $N_{\text{up}}(E_F) = 0.02$ states/eV up to 0.15 states/eV. It appears that these effects could be interpreted either in terms of stronger hybridization with other valence states or charge carriers (holes) localization.

Further detailed study of the band structure of compressed Pr123 system is possible from partial (atomic) densities of states presented in Fig. 4. Generally, the atomic DOS plots are typical for R123 system (see e.g. Refs. [26,27,32–34]). One can notice, that the partial DOS of Pr is dominated by sharp 4f peaks. The Ba atoms generate relatively small DOS in the valence bands. The spectral distributions of Cu(1) and Cu(2) differ slightly: the plane Cu(2) density of states at the Fermi level is significantly higher than that of chain Cu(1) with the considerable weight centered around $-1$ eV. Furthermore, although all the Cu bands extend up to $1.9$ eV, the chain-derived Cu(1) bands extend down only to $-5.8$ eV, while the plane-derived Cu(2) bands extend to $-7.5$ eV. The plane O(2) and O(3) partial densities are practically the same, indicating that orthorhombicity arising from the chains has very little effect on the electronic structure of the CuO$_2$ planes. The plane O(2,3) valence bands extend from roughly $-7$ eV to $2$ eV, that is, in the same range as Cu(2) bands. As the chain oxygens O(4) are considered, the partial DOS is lower than in the case of the O(2) and O(3) oxygens from the planes. The relatively high values of DOS are visible for the apical O(1).

The main advantage of the applied method is that the wave functions and the charge density can be decomposed into atomic contributions. The electronic charge inside the unit cell is distributed either in the interstitial region or in the MT spheres (giving so-called partial charges) where the symmetry decomposition according to $lm$ can be made. These quantities enable us some insight into the charge distribution in the system. Partial charges (in electrons) corresponding to Pr(5s, 5p, 5d, 4f), Ba(6s, 6p, 5d), Cu(4s, 4p, 3d) and O(2s, 2p) majority and minority spin valence states in PrBa$_2$Cu$_3$O$_7$ in ambient pressure are collected in Table 2 and the symmetry decomposition of $p$ and $d$ states is presented separately in Table 3. The analogous data for the Pr123 system after the high-pressure compression is given in Tables 4 and 5.

As could be seen from Tables 2 and 3, the distribution of partial charges of Pr indicate the configuration which is close to $4f^{5}5s^{2}5p^{0}$ of isolated Pr$^{3+}$ ion with some charge moved to d orbitals. The Pr 4f states are spatially confined inside MT sphere. The $p_{x}$, $p_{y}$ and $p_{z}$ states of Pr are not completely filled and they do not exhibit any significant anisotropy. The less occupied Pr 5d states are connected with $d_{xy}$ and $d_{xz}$ symmetries. One can also notice, that some charge is removed from Ba atoms when compared with the nominal Ba$^{2+}$.
ion configuration $5s^25p^6$. It is also visible, that Cu $p$ states are filled, hence, all interactions must be dominated by the $d$ component. For both copper sites, the highest partial charges correspond to $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals, which are nearly filled, what indicates only weak interactions with neighbors. Cu(1) atoms from chains gather the smallest charge in the $d_{z^2}$ and $d_{x^2-y^2}$ symmetries, respectively, as a result of strong interactions with $p_z$ orbitals of apical O(1) and $p_y$ orbitals of chain O(4). Cu(2) atoms in the planes have less charge in the $d_{x^2-y^2}$ state than in $d_{z^2}$ due to strong interactions with O(2) $p_x$ and O(3) $p_y$ states.

Fig. 4. Partial DOS of PrBa$_2$Cu$_3$O$_7$ after the high-pressure compression for the majority (up) and minority (down) spin states. The Fermi level was put at 0 eV.

Table 2
Partial charges corresponding to valence states inside atomic spheres of PrBa$_2$Cu$_3$O$_7$ system for ambient pressure. All data is given in electrons (e).

<table>
<thead>
<tr>
<th></th>
<th>$s$</th>
<th>$p$</th>
<th>$d$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>1.921</td>
<td>5.174</td>
<td>0.354</td>
<td>2.054</td>
</tr>
<tr>
<td>Ba</td>
<td>1.792</td>
<td>4.551</td>
<td>0.117</td>
<td></td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0.222</td>
<td>6.159</td>
<td>8.602</td>
<td></td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.201</td>
<td>6.154</td>
<td>8.657</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>1.549</td>
<td>3.373</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>1.544</td>
<td>3.424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>1.546</td>
<td>3.419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>1.548</td>
<td>3.344</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3
Symmetry decomposition of $p$ and $d$ valence states in PrBa$_2$Cu$_3$O$_7$ in the ambient pressure. All data is given in electrons (e).

<table>
<thead>
<tr>
<th></th>
<th>$p_x$</th>
<th>$p_y$</th>
<th>$p_z$</th>
<th>$d_{xy}$</th>
<th>$d_{xz}$</th>
<th>$d_{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>1.723</td>
<td>1.720</td>
<td>1.731</td>
<td>0.039</td>
<td>0.089</td>
<td>0.034</td>
</tr>
<tr>
<td>Ba</td>
<td>1.525</td>
<td>1.517</td>
<td>1.510</td>
<td>0.024</td>
<td>0.016</td>
<td>0.036</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>2.018</td>
<td>2.059</td>
<td>2.081</td>
<td>1.403</td>
<td>1.649</td>
<td>1.845</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>2.065</td>
<td>2.060</td>
<td>2.029</td>
<td>1.732</td>
<td>1.422</td>
<td>1.853</td>
</tr>
<tr>
<td>O(1)</td>
<td>1.184</td>
<td>1.209</td>
<td>0.981</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>1.000</td>
<td>1.230</td>
<td>1.195</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>1.228</td>
<td>0.958</td>
<td>1.196</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>1.188</td>
<td>0.918</td>
<td>1.239</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In general, a similar scenario of interactions arises from the analysis of partial charges in Pr123 after the high-pressure compression, as can be seen from Tables 4 and 5. However, some redistribution of carriers (and apparently worse transport of charge) takes place as a result of the compression. It is easy to estimate from Tables 4 and 5 that about 0.1 e is shifted into the atomic spheres in the Cu(2)O(2,3) plane at the high pressure, what naturally means the reduction of the same amount of holes (charge carriers). In the frame of the CuO2 plane-derived superconductivity model, which is assumed by a great number of authors, lowered hole concentration could coincide with the lower Tc. One can also notice from Tables 3 and 5 slight reduction of partial charges in Pr with the pz symmetry, as well as in Cu(1) and Cu(2) with dxy and dxz symmetries.

Although the calculated charge distribution seems to be reproduced quite reasonably, it should be stated at this place, however, that the quoted charges depend on the atomic sphere radii chosen to calculate them and may not reflect correctly the ionic charges associated with particular ions. It is well known, that especially in the case of s and p states a large fraction of charge could lie outside the MT sphere.

The differences in the partial charges corresponding to the majority and minority spins are followed by the appearance of the on-site magnetic spin moments. The values of z-axis – projected spin moments μs in PrBa2Cu3O7 before and after the high-pressure compression are listed in Table 6. One can see that the strongly localized Pr magnetic moment μs(Pr) ≈ 1.95 μB, which is responsible for the generation of relatively small magnetic interactions in the CuO2 planes, is reduced by approximately 0.02 μB at the high pressure. This effect is followed by the increase of the on-site magnetic moments in planes (Cu(2), O(2) and O(3) spheres) and the simultaneous slight decrease of magnetic moments in chains (Cu(1) and O(4) spheres). The increased magnetic moments are also visible in the BaO layer (Ba and apical O(1) spheres). Some additional magnetic moment could be also associated with the interstitial region as a result of the compression. Although, the direct interpretation of these results is difficult, one could suspect, however, that the additional magnetic moments in the system, especially in the CuO2 planes, might negatively influence the superconductivity in the Pr123 system under the high pressure.

### 4. Conclusions

We have investigated from the first principles the influence of the high-pressure compression (P ≈ 9 GPa) on the electronic band structure, charge distribution and magnetic moments of the fully oxygenated, ideally stoichiometric PrBa2Cu3O7 system.

The following most important changes were observed as a result of the simulated compression: (i) the reduced total density of states (DOS) at the Fermi level EF, (ii) the increased difference between spin-up and spin-down total DOS in the nearest vicinity of EF (spin splitting), (iii) the lowered occupation of Pr 4f band crossing EF, caused by the shift towards higher energies, (iv) the stronger localization of partial charges in all atomic spheres, (v) the reduced amount of holes in the CuO2 planes and (vi) the enhanced magnetic moments in the system, especially in the CuO2 planes.

The above-listed results indicate the possibility of negative pressure effect on the superconductivity in the stoichiometric PrBa2Cu3O7 system at the sufficiently high hydrostatic pressures. Our calculations are consistent with the theoretically predicted Tc(P) for P ≈ 9 GPa of the optimally doped superconductor PrBa2CuO7 with the initial Tc = 95 K [13].

### Acknowledgments

All calculations were performed at Academic Computer Center in Gdańsk (TASK). Author profited from the fruitful discussions and cooperation in the field of the computational techniques with Dr. R. Laskowski.

### References


Chapter 11

CHARGE DISTRIBUTION AND HYPERFINE INTERACTIONS IN $GdBa_2Cu_3O_7$ FROM FIRST PRINCIPLES

Maciej Łuszczek *
Faculty of Applied Physics and Mathematics
Gdańsk University of Technology
G. Narutowicza 11/12, 80-233 Gdańsk, Poland

Abstract

The electronic band structure, charge distribution and hyperfine interactions, namely, electric field gradients (EFG) and contact terms of hyperfine fields (HFF) in stoichiometric $GdBa_2Cu_3O_7$ ($Gd123$) high-temperature superconductor have been calculated on the first-principles basis using the full-potential linearized augmented plane wave (FP-LAPW) method. The generalized gradient approximation (GGA) was employed to treat the exchange and correlation effects. The Hubbard correction $U$ was applied for $4f$ electrons to account for the strong on-site Coulomb repulsion. The calculated electronic structure and charge distribution is typical for ($rare-\ earth$)123 class of compounds. It was shown that the evaluated strongly localized Gd magnetic moment, which is comparable with the one obtained from the neutron diffraction data, could not effectively influence the neighbors resulting in small itinerant moments in the $CuO_2$ planes. The calculated EFG and HFF parameters are consistent with the Mössbauer measurements. Our results indicate that in the highly correlated $Gd123$ system the applied computational method yields reliable charge distribution to which the EFG and HFF are very sensitive.

PACS 74.72.-h, 71.20.-b, 71.15.Mb, 31.30.Gs.
Keywords: Cuprate superconductors, electronic structure, density functional theory, hyperfine interactions.

1. Introduction

It was demonstrated that in the $YBa_2Cu_3O_{7-\delta}$ ($Y123$) high-temperature superconductor (HTSC) the $Y^{3+}$ ion can be replaced by most of the rare-earth $R^{3+}$ ions [1] without any

*E-mail address: maclu@mif.pg.gda.pl
significant changes in its superconducting properties. The correct understanding of the electronic structure upon the rare-earth substitutions is still a challenge because the coexistence of the magnetism and the superconductivity in this class of compounds is completely different from the behavior of the conventional superconductors.

The charge distribution appears to be a crucial quantity in the analysis of the superconducting properties of the $\text{Y}_{123}$–like systems. The hole concentration in the $\text{CuO}_2$ layers, which are commonly believed to be involved in the superconductivity, depends on the filling of certain $\text{Cu} 3d$ and $\text{O} 2p$ states. Unfortunately, in such complex materials a detailed charge distribution cannot be obtained directly from the experiment (e.g. from the x-ray diffraction data). However, hyperfine interactions, such as electric field gradient (EFG) and hyperfine field (HFF), can be measured by various techniques and provide information on the interaction of a nucleus with the surrounding charge. An interpretation of these measurements allows for precise insight into the electronic and magnetic structure. Therefore, the EFG and HFF measurements seem to be ideally suited for the study of charge distribution in this class of high–$T_c$ superconductors. On the other hand, the accurate electronic structure calculations within density functional theory (DFT) provide the basis for computing either EFG or HFF parameters, what enables direct comparison between theory and experiment.

The local ground state electronic structure can be nicely probed through the EFG at a given nuclear site. In the solid-state physics, this quantity measures the rate of change of the electric field at an atomic nucleus generated by the electronic charge distribution and the other nuclei. The EFG couples with the nuclear electric quadrupole moment of quadrupolar nuclei (with spin quantum number greater than one-half) to generate an effect which can be measured using several spectroscopic methods, such as nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), Mössbauer spectroscopy or perturbed angular correlation (PAC) method. The EFG is defined as the second derivative of the electrostatic potential written as a traceless tensor. The diagonal terms of the EFG tensor with respect to the crystallographic $a$, $b$ and $c$ axes are $V_{aa}$, $V_{bb}$ and $V_{cc}$, respectively. By ordering these components according to their magnitudes we can define $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The EFG is commonly characterized by the largest component $V_{zz}$ and the anisotropy parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$.

The hyperfine field is a precise and essential probe of the magnetic state of a solid and of the quality of theoretical core wave functions. The HFF on a nuclei of an atom may be written as $B_{hf} = B_c + B_{dip} + B_{orb} + B_{lat}$, where $B_c$ is the Fermi contact term, $B_{dip}$ is the dipolar field from the on-site spin density, $B_{orb}$ is the field associated with the on-site orbital moment. $B_{lat}$ is classical dipolar field from all other atoms in the system that carry the magnetic moment. The most important contribution is the Fermi contact term $B_c$, which is the sum of the contributions of valence and core electrons. Usually, nuclear hyperfine fields are associated with local magnetic moments.

In this Chapter we concentrate on the electronic band structure, charge distribution and hyperfine interactions in $\text{GdBa}_2\text{Cu}_3\text{O}_7$ high-temperature superconductor because the reliable experimental results are available [2], [3], [4], [5] and so the direct comparison with our computational approach is possible.
2. Computational Details

All calculations were performed within the generalised gradient approximation (GGA) [6], which provides an improved description of exchange and correlation effects in solids in comparison with the standard local-spin density approximation (LSDA). The local orbital extension (LO) of the full-potential linearized augmented-plane wave (FP-LAPW) method [7], [8] was applied. The well-known WIEN2k code [9], [10] was used for the electronic structure calculations. Approximately 1400 LAPW functions plus LOs were used. The crystallographic data for \( \text{GdBa}_{2}\text{Cu}_{3}\text{O}_{7-\delta} \) with \( P m m m \) symmetry, collected in Ref. [11], were used as the input. Atomic sphere radii of 2.30, 2.30, 1.90, and 1.55 a.u. were taken for Gd, Ba, Cu, and O, respectively. The plane-wave cutoff \( R_{\text{min}}K_{\text{max}} = 6.0 \) was chosen, where \( R_{\text{min}} \) denotes the smallest atomic sphere radius and \( K_{\text{max}} \) gives the magnitude of the largest \( K \) vector in the plane-wave expansion. Self-consistency was obtained using a set of 16 special \( k \) points in the irreducible Brillouin zone (IBZ) with the charge density taken as a criteria of convergence (the “charge distance” of the order of \( 10^{-5}e \) between the successive iterations was reached).

The core and valence states were treated self-consistently, the former relativistically in an atomic-like approximation [12] and the later — scalar relativistically with spin-orbit interactions included in a second-variational procedure [13]. The starting (free-atom) electron configurations of the constituent atoms were as follows: \( \text{Gd} [Xe] 4f^7 5d^1 6s^2, \text{Ba} [Xe] 6s^2, \text{Cu} [Ar] 3d^9 4s^2 \) and \( \text{O} [He] 2s^2 2p^4 \). The GGA plus Hubbard parameter \( U(\text{GGA+U}) \) approach [14] was employed to account for the strong on-site Coulomb repulsion of the \( 4f \) electrons in Gd. The \( U_{\text{Gd}} = 0.4 \) \( R_y \) and \( J_{\text{Gd}} = 0.07 \) \( R_y \) parameters were applied (the same values were successfully used for \( 4f \) states in the previous study of the \( \text{DyBa}_2\text{Cu}_3\text{O}_7 \) and \( \text{TbBa}_2\text{Cu}_3\text{O}_7 \) systems [15], [16]). It was reported in the literature that conventional band structure calculations can quite properly reproduce many physical properties of the metallic (doped) HTSC and \( U_{\text{Cu}} \) parameter could play an important role mainly in the case of the underdoped materials [17]. In this study we assumed the optimally doped (metallic) character of the \( \text{Gd}123 \) system and thus this correction for Cu \( 3d \) states was not applied. The modified tetrahedron method of Blöchl et al. [18] was used to determine the density of states (DOS). The electric field gradients (EFG) can be calculated directly from the self-consistent charge density by solving Poisson’s equation without further approximations, as it was firstly demonstrated by Blaha et al. [19]. The hyperfine field (HFF) calculations were performed using relativistic formula given by Breit [20]. The employed implementation of FP-LAPW method enable to determine the relativistic contact contribution \( B_c \), obtained by the averaging of spin over a small region (with the size described by the Thomson radius \( r_T = Ze^2/mc^2 \)) around the nucleus.

3. Results and Discussion

The calculated electronic structure of \( \text{GdBa}_2\text{Cu}_3\text{O}_7 \), with the dominant \( \text{Cu}(1) 3d - \text{O}(4) 2p \) (CuO chain-derived) and \( \text{Cu}(2) 3d - \text{O}(2,3) 2p \) (CuO\(_2\) plane-derived) bands crossing the Fermi level, exhibits the metallic character, as expected, and the bands are similar to those established in the \( Y123 \) system [21], [22]. The total density of states (DOS) of \( \text{Gd}123 \) is presented in Figure 1. One can notice some narrow high-density peaks, cor-
responding to $Gd\ 4f$-derived bands, which are shown separately in Figure 2. Noteworthy, there is no fractional occupation of $Gd\ 4f$ states at the Fermi level ($E_F$) in the GGA calculations, what was recently observed for $Dy\ 4f$ states in $Dy123$ system [15], resulting in an atomic-like $Gd^{3+}$ ion behavior. The $U_{Gd}$ parameter produces the additional Hubbard splitting between the occupied and empty $4f$ states. In the both methods the $Gd\ 4f$ minority spin states are entirely above the Fermi energy.

![Graph of total density of states (DOS) for majority (up) and minority (down) spin states in $GdBa_2Cu_3O_7$ system from GGA and GGA+$U$ calculations. The Fermi level was put at 0 eV.](image1)

Figure 1. The total density of states (DOS) for majority (up) and minority (down) spin states in $GdBa_2Cu_3O_7$ system from GGA and GGA+$U$ calculations. The Fermi level was put at 0 eV.

The details of the total DOS in the nearest vicinity of $E_F$ obtained from GGA and GGA+$U$ calculations are shown in Figure 3. At a first glance there are some differences between the both approaches. As can be seen, the noticeable spin splitting of bands at the Fermi level occurs only in the GGA calculations. The GGA+$U$ calculations also give the splitting of DOS but it extends roughly below $-50\ meV$ and is not supposed to affect the superconductivity (it is well known that the energy gap $2\Delta$ in the high-$T_c$ copper oxide superconductors is roughly equal $50\ meV$ [23]). The same effect was previously reported for $Dy123$ system in the analogous GGA+$U$ study [15]. What is more, the $Gd123$ system exhibits slightly higher value of density of states at the Fermi level than $Dy123$, that is,
Figure 2. The positions of majority (up) and minority (down) Gd 4f bands from GGA and GGA+U calculations. The Fermi level was put at 0 eV.

$N_{Gd123}(E_F) = 3.50 \text{ states/eV}$ and $N_{Dy123}(E_F) = 3.16 \text{ states/eV}$ what could imply slightly better superconducting properties of this compound. Indeed, it is known from the experiment that the superconducting transition temperature $T_c$ in $R123$ shows a week increase with the size of the $R^{3+}$ ion [24]. Taking the above facts into considerations, the use of GGA+U seems to be a better choice in the case of Gd123 system.

The atomic-decomposed (partial) DOS characteristics from the GGA+U approach are presented in Figure 4. As stated before, the partial DOS of Gd in Gd123 is dominated by 4f peaks. Ba atoms generate relatively small DOS in the valence bands and unoccupied states are shifted upwards by approximately 3.5 eV above $E_F$. The plane $Cu(2)$ density of states at the Fermi level is significantly higher than that of chain $Cu(1)$ with the considerable weight centered around $-1$ eV. All the $Cu$ bands extend to very similar positions at the top of the bands (2 eV). However, the chain-derived $Cu(1)$ bands extend down only to (approximately) $-5.5$ eV, while the plane-derived $Cu(2)$ bands extend to $-7$ eV. As could be seen from Figure 4, the plane $O(2)$ and $O(3)$ partial densities are practically identical, indicating that orthorhombicity arising from the chains has very little effect on the electronic structure of the $CuO_2$ planes. The plane $O(2,3)$ valence bands extend from roughly...
Figure 3. Details of total DOS of GdBa$_2$Cu$_3$O$_7$ systems in the nearest vicinity of the Fermi level for the majority (up) and minority (down) spin states obtained from the GGA and GGA+U calculations. The Fermi level was put at 0 eV.

$-7 \text{eV}$ to $2 \text{eV}$, that is, in the same range as Cu$(2)$ bands. As the chain oxygens O$(4)$ are considered, the partial DOS is lower than in the case of the O$(2)$ and O$(3)$ oxygens from the planes. These results are generally consistent with the previously reported calculations of Y$_{123}$-like systems [15], [16], [25], [26].

In the applied method of calculations the electronic charge inside the unit cell is distributed either in the interstitial region or in the atomic spheres giving so-called partial charges. Thus, the symmetry decomposition according to $lm$ numbers can be made [9], [10]. Partial charges (in electrons) corresponding to Gd$(5s, 5p, 5d, 4f)$, Ba$(6s, 5p, 5d)$, Cu$(4s, 4p, 3d)$ and O$(2s, 2p)$ majority and minority spin valence states in GdBa$_2$Cu$_3$O$_7$ are collected in Table 1 and the symmetry decomposition of $p$ and $d$ states is presented in Table 2.

As could be seen from Table 1, only small leakage of Gd$4f$ charge from the atomic sphere is visible, what means that $4f$ states are quite well spatially confined and therefore they cannot effectively hybridize with the other valence electrons. The partial charges of Gd correspond to almost nominal $4f^{7} 5s^{2} 5p^{6}$ configuration of isolated Gd$^{3+}$ ion with about
Figure 4. Partial DOS of $GdBa_2Cu_3O_7$ system for the majority (up) and minority (down) spin states in the GGA+$U$ approach. The Fermi level was put at 0 eV.
Table 1. Calculated partial charges in $GdBa_2Cu_3O_7$ system. All data is given in electrons ($e$).

<table>
<thead>
<tr>
<th></th>
<th>$s$</th>
<th>$p$</th>
<th>$d$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Gd$</td>
<td>1.99</td>
<td>5.51</td>
<td>0.39</td>
<td>6.97</td>
</tr>
<tr>
<td>$Ba$</td>
<td>1.79</td>
<td>4.55</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>$Cu(1)$</td>
<td>0.22</td>
<td>6.16</td>
<td>8.31</td>
<td></td>
</tr>
<tr>
<td>$Cu(2)$</td>
<td>0.20</td>
<td>6.16</td>
<td>8.66</td>
<td></td>
</tr>
<tr>
<td>$O(1)$</td>
<td>1.55</td>
<td>3.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(2)$</td>
<td>1.54</td>
<td>3.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(3)$</td>
<td>1.54</td>
<td>3.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(4)$</td>
<td>1.55</td>
<td>3.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.4 $e$ shifted to $d$ orbitals. One can notice that $p_x$, $p_y$ and $p_z$ states of $Gd$ are filled without significant anisotropy and that the charges of $d_{x^2}$ and $d_{yz}$ symmetries are significantly smaller than that of the $d_{x^2−y^2}$ and $d_{xy}$, $d_{xz}$ (see Table 2). In the $Ba$ atomic sphere some part of the valence charge is moved to $5d$ states, as well, when compared with the $5s^25p^6$ configuration of $Ba^{2+}$ ion. For both copper sites, the highest partial charges correspond to $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals, which are nearly filled, what means that their interactions with the neighbors are weak. The chain $Cu(1)$ atoms gather the smallest charge in the $d_{x^2}$ and $d_{y^2}$ symmetries as a result of strong interactions with $p$ orbitals of $O(1)$ and $O(4)$, whereas the $Cu(2)$ atoms (from the planes) have less charge in the $d_{x^2−y^2}$ state than in $d_{z^2}$ due to strong interactions with the $O(2)$ and $O(3)$ atoms. The $O(2)$ sphere is involved in strong interaction mainly in $x$ direction (the $p_x$ partial charge is the smallest one). On the other hand, for the $O(3)$ position the interactions have mostly $y$ character. Consequently, the strongest interactions can be determined along the $z$ axis for the apical $O(1)$ atoms what is indicated by the smallest value of charge with the $p_z$ symmetry. In the case of the chain $O(4)$ atoms the smallest $p$ component is visible for $y$ direction. These results are consistent with the previously reported charge distribution for the $Y123$ [27] and $Dy123$ [15] HTSC. One should be aware, however, that the quoted charges depend on the atomic sphere radii chosen to calculate them and they may not reflect correctly the ionic charges associated with particular ions. This is mainly because of the $s$ and $p$ states for which a large fraction of charge lies outside the atomic sphere.

Table 3 summarizes the EFG tensor, the principal component $V_{zz}$ and the asymmetry parameter $\eta$. The value of $V_{zz} = -8.41\cdot10^{21} V/m^2$ calculated for $Gd$ position is larger than the experimental values of $V_{zz} = -(5.1\pm0.2)\cdot10^{21} V/m^2$ [4] and $V_{zz} = -4.9\cdot10^{21} V/m^2$ [5] derived from Mössbauer measurements. On the other hand, the asymmetry parameter $\eta = 0.41$ obtained from our calculations is equal (within the experimental error) to the experimental value of $\eta = 0.42\pm0.03$ from Ref. [4] and is slightly smaller than $\eta = 0.6\pm0.1$ and $\eta = 0.57\pm0.02$ reported for the orthorhombic phase in Refs. [2] and [5], respectively. As the copper and oxygen positions are concerned, the calculated EFG parameters are generally consistent with those either calculated or found experimentally in the parent high-temperature superconductor $YBa_2Cu_3O_7$ (see Ref. [27] and references therein). It was demonstrated that the anisotropy in the charge density around the oxygen atoms is directly proportional to the corresponding EFG. The principal component is positive for all oxygens.
Table 2. Symmetry decomposition of $p$ and $d$ valence states in $GdBa_2Cu_3O_7$. All data is given in electrons (e).

<table>
<thead>
<tr>
<th></th>
<th>$p_x$</th>
<th>$p_y$</th>
<th>$p_z$</th>
<th>$d_{z^2}$</th>
<th>$d_{x^2-y^2}$</th>
<th>$d_{xy}$</th>
<th>$d_{xz}$</th>
<th>$d_{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Gd$</td>
<td>1.835</td>
<td>1.833</td>
<td>1.840</td>
<td>0.040</td>
<td>0.099</td>
<td>0.037</td>
<td>0.108</td>
<td>0.102</td>
</tr>
<tr>
<td>$Ba$</td>
<td>1.526</td>
<td>1.517</td>
<td>1.509</td>
<td>0.025</td>
<td>0.016</td>
<td>0.037</td>
<td>0.024</td>
<td>0.017</td>
</tr>
<tr>
<td>$Cu(1)$</td>
<td>2.019</td>
<td>2.062</td>
<td>2.082</td>
<td>1.402</td>
<td>1.645</td>
<td>1.846</td>
<td>1.845</td>
<td>1.863</td>
</tr>
<tr>
<td>$Cu(2)$</td>
<td>2.066</td>
<td>2.062</td>
<td>2.029</td>
<td>1.732</td>
<td>1.417</td>
<td>1.854</td>
<td>1.827</td>
<td>1.826</td>
</tr>
<tr>
<td>$O(1)$</td>
<td>1.185</td>
<td>1.211</td>
<td>0.981</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(2)$</td>
<td>1.007</td>
<td>1.225</td>
<td>1.191</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(3)$</td>
<td>1.223</td>
<td>1.004</td>
<td>1.191</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O(4)$</td>
<td>1.187</td>
<td>0.923</td>
<td>1.242</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and points in the direction of the largest anisotropy. As can be noticed from Table 3, the largest anisotropy parameter is found for the chain $O(4)$ position yielding the highest EFG among oxygens and pointing in the $b$ direction. This is because the $O(4)$ site has copper neighbors only in the $y$ direction (i.e. along the $b$ axis) leading to large $V_{bb}$ and relatively small $\eta = 0.28$. The $V_{zz}$ of plane $O(2)$ and $O(3)$ positions point into $a$ and $b$ directions, respectively. The smallest anisotropy parameter corresponds to the $O(1)$ site for which the main EFG component points into the $c$ direction. For the $Cu(1)$ position the $c$ component $V_{cc}$ is very small, while $V_{aa}$ and $V_{bb}$ have similar values with opposite signs leading to large asymmetry parameter $\eta = 0.80$. On the other hand, the EFG on $Cu(2)$ site points into the $c$ direction while $V_{aa}$ and $V_{bb}$ are similar giving small value of $\eta = 0.14$.

The interaction between nuclei and electrons can be also described by an effective field called hyperfine field (HFF). The values of the Fermi contact term $B_c$ on different sites and the corresponding magnetic moments are collected in Table 4. In our calculations $Gd$ magnetic moment of $\mu_{Gd} \approx 6.93 \mu_B$ is found, which is in a very good agreement with the experimental value of $\mu_{Gd} = (7.4 \pm 0.6) \mu_B$ from the neutron diffraction data [28]. The $4f$ spin moment polarizes the valence bands, what gives rise to small itinerant moments in the system, as well. As can be noticed, the strong localized magnetic moment of $Gd$ is responsible for the generation of relatively small magnetic interactions, mainly

Table 3. Calculated electric field gradient (EFG) components (in $10^{21}$ V/m$^2$) for $GdBa_2Cu_3O_7$ superconductor.

<table>
<thead>
<tr>
<th>Position</th>
<th>$V_{zz}$</th>
<th>$\eta$</th>
<th>$V_{aa}$</th>
<th>$V_{bb}$</th>
<th>$V_{cc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Gd$</td>
<td>-8.41</td>
<td>0.41</td>
<td>2.48</td>
<td>5.93</td>
<td>-8.41</td>
</tr>
<tr>
<td>$Ba$</td>
<td>-8.80</td>
<td>0.98</td>
<td>-8.80</td>
<td>0.070</td>
<td>8.73</td>
</tr>
<tr>
<td>$Cu(1)$</td>
<td>-6.42</td>
<td>0.80</td>
<td>-6.42</td>
<td>5.78</td>
<td>0.64</td>
</tr>
<tr>
<td>$Cu(2)$</td>
<td>-5.23</td>
<td>0.14</td>
<td>2.99</td>
<td>2.24</td>
<td>-5.23</td>
</tr>
<tr>
<td>$O(1)$</td>
<td>13.09</td>
<td>0.19</td>
<td>-5.32</td>
<td>-7.77</td>
<td>13.09</td>
</tr>
<tr>
<td>$O(2)$</td>
<td>12.45</td>
<td>0.21</td>
<td>12.45</td>
<td>-7.53</td>
<td>-4.92</td>
</tr>
<tr>
<td>$O(3)$</td>
<td>12.44</td>
<td>0.20</td>
<td>-7.48</td>
<td>12.44</td>
<td>-4.96</td>
</tr>
<tr>
<td>$O(4)$</td>
<td>17.83</td>
<td>0.28</td>
<td>-6.45</td>
<td>17.83</td>
<td>-11.38</td>
</tr>
</tbody>
</table>
500 Maciej Łuszczek

Table 4. The calculated Fermi contact term $B_c$ of HFF (in units of $kG$) and the corresponding magnetic moments (in $\mu_B$) in the atomic spheres in $\text{GdBa}_2\text{Cu}_3\text{O}_7$.

<table>
<thead>
<tr>
<th>Position</th>
<th>$B_c$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>268.117</td>
<td>6.9291</td>
</tr>
<tr>
<td>Ba</td>
<td>-0.494</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>-1.167</td>
<td>-0.0003</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>-0.424</td>
<td>-0.0039</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.279</td>
<td>-0.0018</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.384</td>
<td>-0.0093</td>
</tr>
<tr>
<td>O(3)</td>
<td>-0.515</td>
<td>-0.0096</td>
</tr>
<tr>
<td>O(4)</td>
<td>-0.582</td>
<td>-0.0014</td>
</tr>
</tbody>
</table>

in the $\text{CuO}_2$ planes. The calculated total contact contribution at the $\text{Gd}$ position is $B_c \simeq 268$ $kG$ and it is slightly underestimated when compared with the experimental values of $B_{hf} = (290 \pm 30)kG$ [3], [4] or $B_{hf} \simeq 302$ $kG$ [2]. This difference might originate from the smaller theoretical $Gg$ magnetic moment (as compared with the experiment) and the neglected dipolar and orbital contributions to the HFF. Noteworthy, it is obvious that the assumption of the simple proportionality of the hyperfine field to the local magnetic moments seems not to be justified in the cases of the investigated $\text{GdBa}_2\text{Cu}_3\text{O}_7$ system.

4. Conclusion

In this work the electronic band structure, charge distribution and hyperfine interactions in stoichiometric $\text{GdBa}_2\text{Cu}_3\text{O}_7$ high-temperature superconductor have been calculated on the first-principles basis. The electronic structure of $\text{Gd123}$ is typical for this class of compounds. Also charge distribution is similar to analogous $\text{R123}$ systems [15], [27]. The presented results show that the evaluated strong on-site magnetic moment of $\text{Gd}$, which is in a good agreement with the neutron diffraction data [28], could not effectively influence the neighbors resulting in small itinerant moments in the $\text{CuO}_2$ planes. The calculated values of electric field gradient (EFG) and hyperfine field (HFF) parameters, which may be treated as a measure of the correctness of the applied theoretical approach, are quite well reproduced and consistent with the Mössbauer measurements [2], [3], [4], [5].

In conclusion, a good agreement between the $ab\ initio$ calculations and the experiment has been found, what indicates that in the highly correlated $\text{GdBa}_2\text{Cu}_3\text{O}_7$ system the applied computational method yields reliable charge distribution to which the EFG and HFF are very sensitive.

Acknowledgements

The Academic Computer Center in Gdańsk (TASK), where all the calculations were performed, is acknowledged.
References


