Electronic structure and phonon behaviour under pressure in YBa$_2$Cu$_4$O$_8$

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Abstract

The electronic structure of the high-$T_c$ superconductor YBa$_2$Cu$_4$O$_8$ and its change under pressure have been determined within the local density approximation (LDA) to density functional (DF) theory using the full-potential Linearized Muffin Tin Orbital (LMTO) method. The pressure dependence of the energy positions of the plane-derived and chain-derived bands which lie close to and cross the Fermi energy indicates the existence of a hole transfer from the CuO chains and ionic elements to the CuO$_2$ planes with a rate that diminishes as pressure increases. The behaviour of the frequencies of the Cu(2) and apical-oxygen modes under pressure which have recently been described in Raman measurements are studied in the framework of the Frozen Phonon Approximation. The agreement with experiment shows that the intricate mechanisms involved as pressure varies (charge transfer and changes to the lattice dynamical properties) can be well described by state of the art electronic structure calculations which treat the many-body Coulomb interactions within the LDA.

1. Introduction

The high-$T_c$ superconductor YBa$_2$Cu$_4$O$_8$ (Y124) is closely related to the very much studied compound YBa$_2$Cu$_3$O$_{6.9}$ (Y123). It has basically the same structure, but with two Cu(1)–O(1) chains running between the Ba–O(4) planes instead of one, and is described by a base-centered orthorhombic unit cell. Although the crystal structures of both compounds are similar, there exist significant differences between them.

The pressure dependence of $T_c$ in Y124 is of particular interest, since it exhibits a very large positive initial derivative $dT_c/dP = 5.5$ K/GPa up to 4 GPa [1], and $T_c$ has a maximum as a function of the applied pressure [2]. The holes created in the two dimensional CuO$_2$ planes by self-doping through the CuO chains and ionic reservoir are responsible for superconductivity, and it is now well established that there is a direct correlation between $T_c$ and the density of these hole carriers [3–5]. The pressure-induced structural changes of Y124 have been investigated by neutron [6] and X-ray [7] diffraction techniques in the pressure ranges 0–0.632 GPa and 0–4.65 GPa, respectively. A movement of the apex oxygen from the CuO chains to the CuO$_2$ planes with pressure has been observed with a higher compressibility than that of the $c$-axis. This has been
taken as a signature of a hole transfer from the chains to the planes, which has been supported by Hall effect [8], NMR and NQR [9] measurements. Using atomistic simulation techniques, Zhang and Catlow [10] suggested that the Cu(2)–O(4) bond length may be a good indicator of charge transfer but not of the pressure dependence of $T_c$. They found that there exist anomalous structural changes in the CuO$_2$ plane above pressure of 5 GPa, which may cause charge carrier redistribution in the CuO$_2$ plane.

Gupta et al. [11] on the other hand, using the tight binding recursion method and comparing the pressure-induced charge redistribution in Y123 and Y124 assign an unimportant role to the plane-Cu–apical oxygen bond in the pressure dependence of $T_c$, even rejecting the possibility of obtaining an approximate picture of charge transfer on the basis of a variation of bond lengths alone as a function of pressure.

The effect of pressure on the Raman modes of Y124 has been investigated up to 16 GPa at room temperature by Kakihana et al. [12]. They observed an anomalous pressure dependence of Raman shifts of the mode at 147 cm$^{-1}$ which has been assigned to the displacement of the Cu(2) in the CuO$_2$ plane along the z-axis. This pressure-induced Raman shift was observed to behave nonlinearly in almost the same way as $T_c$, while the frequencies of the other Raman modes increase almost linearly with increasing pressure. It was suggested that this anomalous behavior of the Cu(2) mode might be a signature of a change in the electronic state of the CuO$_2$ plane which can be related to $T_c$.

Calculations of the electronic structure and related properties of YBa$_2$Cu$_4$O$_8$ at atmospheric pressure have been performed within LDA using the full-potential Linearized Augmented Plane Wave method (FP-LAPW) [13–15], obtaining band structures in good agreement with each other for this material. While the full-potential Linearized Muffin Tin Orbital (FP-LMTO) method has been successfully applied to the study of Y123 [16] and several other high-$T_c$ superconductors [17–19], detailed results of the band structure of YBa$_2$Cu$_4$O$_8$ have not been presented although recently model Hamiltonians were obtained based on this formalism [20].

In this paper, we present results of the electronic structure and Raman active Cu(2) and apical oxygen phonon modes of YBa$_2$Cu$_4$O$_8$ under pressure, at those pressures where experimental structures are known (0, 3.2 and 4.65 GPa), as obtained within LDA based on the FP-LMTO method. The pressure dependence of the energy positions relative to $E_F$ of plane and chain-derived bands shows the existence of a hole transfer from the CuO chains and ionic reservoir to the CuO$_2$ planes whose rate diminishes with the pressure increase. The behaviour of the Cu(2) and apical oxygen modes as pressure varies is studied in the framework of the Frozen Phonon Approximation. In the examined pressure range the frequency of the two modes has a linear change in rather good agreement to what is observed in Raman measurements. No attempts were made to couple Cu(2) and oxygen modes.

As pressure varies, intricate mechanisms (of charge transfer, structural modifications and changes to lattice dynamical properties) are set into play. The calculations here presented thus corroborate once more the important issue that the LDA (although it represents a crude approximation to the many-body Coulomb interactions) can describe the static density response of complex systems like high-temperature superconductors under pressure.

2. Method of calculation

For the calculation of the electronic structure and the Raman active Cu(2) and apex oxygen modes we used a fast and precise full-potential linear muffin-tin orbital (FP-LMTO) code by Methfessel [21,22] within the LDA and the Hedin–Lundqvist exchange-correlation potential. In the FP-LMTO, no shape approximations are made for either the charge density or the potential. As is customary for an LMTO approach, the basis for the wave function consists of atom-centered Hankel functions which are augmented by numerical solutions of the radial one electron equation within the nonoverlapping atomic spheres. The charge density is represented in the interstitial region by fitting a linear combination of Hankel functions to the values and slopes on the sphere boundaries. To provide sufficient variational freedom, it is essential in the method to extend the basis using LMTO’s with various localizations. The envelope function decays as $e^{-\kappa r}$, where $-\kappa^2$ is the kinetic energy of the Hankel function envelope.
The calculations were carried out in two panels. The following orbitals were taken as valence band electrons: Y 4d and 5s, Ba 5p and 6s, Cu 3d and 4s, and O 2s and 2p. The Y 4s and 4p, Ba 5s and Cu 3s and 3p were included as semicore. We have used $\kappa^2 = -0.01$, $-1.0$ and $-2.3$. The basis set included 247 LMTO's per cell and 52 irreducible points were used (plus linear tetrahedral interpolation) to sample the Brillouin zone (corresponding to $6 \times 6 \times 6$ regular divisions along the basis vectors for the reciprocal lattice $b_1$, $b_2$ and $b_3$, respectively). The muffin-tin (MT) radii were 2.80, 3.3, 1.82 and 1.66 au for Y, Ba, Cu and O respectively, for the atmospheric pressure structure. Empty spheres were added (at the planes parallel to CuO$_2$ planes containing CuO chains, containing Y and between the two CuO chains) in order to achieve better space filling. The resulting sphere packing ratio ($V_{MT}/V_{total}$) was around 51.7%. The muffin-tin sphere radii were scaled to preserve this packing ratio at all pressures.

Measurements of the lattice parameters and atomic positions in Y124 at different pressures have been made by Nelmes et al. [7]. We have used their data at $P = 0$, 3.2 and 4.65 GPa. For the frozen-phonon calculation presented below we have calculated the total energy for a sufficient number of displacements ranging up to 3% of the lattice constant $a$. A second order least-squares fit was applied, and the phonon frequencies were derived.

3. Results and discussion

The calculated valence band structure of Y124 at atmospheric pressure is shown in Fig. 1. In order to make a detailed comparison of our band structure with LAPW calculations, we have plotted the energy bands in the same high symmetry directions of Ref. [14]. As can be seen, our band structure is in good agreement with earlier LAPW calculations [13–15]. This band structure is similar to that of Y123 [16], but simpler near $E_F$. The flat 1D Cu(1)–

![Fig. 1. Band structure of YBa$_2$Cu$_4$O$_8$.](image)
CuO chains

Energy (eV)

0.5

-0.5

-1

G X S Y G

CuO2 planes

Energy (eV)

-1

0.5

-0.5

-0.2

G X S Y G

Fig. 2. Projected band structure of YBa$_2$Cu$_4$O$_8$ indicating the CuO chain and CuO$_2$ plane states contributions to each band state.

O(1) $d_{p\pi}$ antibonding band which lies near $E_F$ in Y123 is absent basically due to the change in the local symmetry of the O(1) atoms. This reduces the density of states near $E_F$ to one half of that in Y123. There is one additional band which originates from the second CuO chain. Four bands cross $E_F$ along the X–S line, two of them are associated with the CuO$_2$ planes and the other two with the CuO chains. The orbital character of these bands can be seen in the projected band structure shown in Fig. 2, which allows us to see the chain and plane states contributions of each band state.

Extended van Hove singularities (vHs) in the electronic structure appear in our calculation below $E_F$ in the neighborhood of the X and Y points, extended along the G–X and G–Y, respectively. The vHs at X has a binding energy of 0.1 eV (CuO$_2$ plane band) and the CuO chain band lies at 0.39 eV below $E_F$. The vHs at Y lies 0.28 eV below $E_F$. A significant difference between our results and those of Ref. [14] is observed at Y below $E_F$. The occurrence of vHs in Y123 and Y124 have been reported by Gofron et al. [23] using angle-resolved photoemission (ARPES). In Y124 the vHs was found at a binding energy of 0.019 eV at the Y point, much closer to the Fermi energy than our calculated value.

In all our pressure studies we have used X-ray structural data at $P = 0$, 3.2 and 4.65 GPa reported in Ref. [7]. The effect of pressure on the electronic structure of Y124 is seen in Fig. 3, which presents the band structure along G–X–S directions for these different pressures. A very important feature is clearly seen: the two bands at the X point below $E_F$ move with respect to the Fermi level. Under applied pressure, while the vHs corresponding to the CuO$_2$ planes moves towards the Fermi level (from $-0.1$ eV at $P = 0$ GPa to $-0.068$ eV at $P = 4.65$ GPa), the band corresponding to the CuO chains moves away from $E_F$ (from $-0.39$ eV at $P = 0$ GPa to $-0.44$ eV at $P = 4.65$ GPa). This indicates the existence of a hole transfer to the CuO$_2$ planes. A quantitative determination of charge transfer is not straightforward within our scheme; it has been the subject of many experimental investigations and is still extensively debated [8,2,9].

Nelmes et al. [7] pointed out that amongst the principal structural changes under pressure, that of Cu(2)–O(4) bond length stands out. At 4.65 GPa, the Cu(2)–O(4) bond length is reduced by 3% (twice that of c) but the rate of its change with pressure is

Fig. 3. Band structure of YBa$_2$Cu$_4$O$_8$ along G–X–S directions in the BZ for structures at different pressures.
decreasing as pressure increases. This supports a suggestion of a common underlying relationship between \( T_c \) and Cu(2)–O(4) distance. In Fig. 4 we show the pressure dependence of the energy positions of the plane and chain bands with energies close to the Fermi level. At low pressures (between 0 and 3.2 GPa) there are big shifts indicating extensive hole transfer which becomes less pronounced between 3.2 and 4.65 GPa. This provides some evidence that the structural changes can be correlated with the hole transfer and the non-linear pressure dependence observed for \( T_c \) above 4 GPa. However, this is not a conclusive probe and further calculations using high pressure structures are necessary.

The pressure dependence of the Raman O(4) and Cu(2) modes were studied in the framework of the Frozen Phonon Approximation. We have neglected the coupling between these ions and others, so our results must be taken as semiquantitative. The pressure dependences of both modes are shown in Fig. 5. For the O(4) mode (Fig. 5a), we have obtained a frequency of 493 cm\(^{-1}\) at ambient pressure, in very good agreement with Raman measurement of 500 cm\(^{-1}\) [12]. The pressure derivative for this mode is 4.36 cm\(^{-1}/\)GPa, which is also in fairly good agreement with 3.83 cm\(^{-1}/\)GPa reported in Ref. [12]. On the other hand, for the Cu(2) mode (Fig. 5b), we have obtained a frequency of 124.72 cm\(^{-1}\) at ambient pressure, while the experimentally determined frequency by Raman is 147 cm\(^{-1}\). The pressure derivative for this mode is also small compared with its experimental value. As explained above, these discrepancies can be related to the neglect of coupling between Cu(2) and O ions. In this pressure range, the pressure dependence of the two modes is linear in a way similar to that observed in Raman scattering experiments. The Cu(2) mode deviates from linearity at pressures exceeding 6 GPa [12].

In conclusion, we have presented results for the electronic structure and Raman active Cu(2) and O(4) phonon modes of YBa\(_2\)Cu\(_4\)O\(_8\) under pressure. The pressure dependence of the energy positions of the Cu–O plane and chain bands close to \( E_F \) shows
the existence of a non-linear hole transfer to the CuO$_2$ planes. Although we present some evidence of a possible correlation between this charge transfer and the Cu(2)–O(4) bond length, an experimental determination of high pressure structures is necessary in order to make calculations at pressures higher than 5 GPa. These calculations could also elucidate if the Cu(2) mode has a non-linear frequency increase.

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