Disorder-induced localisation and suppression of superconductivity in YSr 2 Cu 3 O 6+ x

Andrea Gauzzi, Gianni Profeta, Alessandra Continenza, Fabio Bernardini, Sandro Massidda

Disorder-induced localisation and suppression of superconductivity in $YSr_2Cu_3O_{6+x}$

Andrea Gauzzi

IMPMC, Sorbonne Université, UMR7590 CNRS, IRD, MNHN, 4, place Jussieu, 75005 Paris, France

E-mail: `andrea.gauzzi@sorbonne-universite.fr`

Gianni Profeta, Alessandra Continenza

Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila, 67010 Coppito, Italy

Fabio Bernardini, Sandro Massidda

Dipartimento di Fisica, Università di Cagliari, 09042 Monserrato, Italy

Abstract.
By means of *ab initio* calculations within the local density approximation to density functional theory, we investigate the electronic structure of the 60 K superconductor $YSr_2Cu_3O_{6+x}$ (YSCO). We focus on the effects of the Sr/Ba substitution and on the main structural modifications induced by this substitution experimentally found in the Sr compound, namely the tetragonal symmetry and the oxygen disorder in the basal plane. In the calculations, this disorder is simulated by using a supercell approach. Due to band structure effects, we find a larger stabilisation free energy of the orthorhombic structure in $YBa_2Cu_3O_{6+x}$ (YBCO). In YSCO, the tetragonal disordered phase is found to be stabilized by oxygen overdoping ($x > 1$) and by sufficiently large mass-enhancement factors, $\gamma > 5$. The analysis of the atomic site projected density of states suggests that oxygen disorder in the CuO basal planes of YSCO induces hole localisation, which accounts for the large 30 K reduction of T_c with respect to YBCO.

Keywords: superconductivity, first-principles calculations, charge localisation

1. Introduction: role of oxygen disorder on superconductivity in cuprates

More than thirty years after the discovery of high-temperature superconductivity (HTSC) in cuprates [1], the explanation of this extraordinary phenomenon remains one of the great challenges of condensed matter physics. One difficulty is the complex crystal structure combined with chemical disorder, two characteristic features of these superconductors. Typically, this disorder is caused by oxygen doping in the pristine insulating phase, which is required to create mobile holes in the CuO_2 planes and thus to induce superconductivity. It is therefore important to investigate the effects of oxygen

disorder on the electronic properties, considering that the local crystal structure may differ from the average one probed by diffraction techniques.

In the present work, we address this issue in the case of $YSr_2Cu_3O_{6+x}$ (YSCO) [2, 3, 4, 5], the counterpart of the well-known $YBa_2Cu_3O_{6+x}$ (YBCO) compound where Ba is fully substituted by Sr. Contrary to the expectation that the chemical pressure exerted by the comparatively small Sr ion should enhance superconductivity, in YSCO the critical temperature, T_c, is unexpectedly reduced from 90 K to 60 K. This result is surprising considering that the above substitution does not perturb the superconducting CuO_2 planes and successfully induces the desired chemical pressure effect [4]. Here, we consider the possibility that the above reduction is due to the disorder of the oxygen atoms in the basal planes in superconducting $YSr_2Cu_3O_{6+x}$ for $x \approx 1$ [4, 5, 6, 7], which contrasts the configuration of well-ordered CuO chains in optimally doped $YBa_2Cu_3O_{6+x}$ for an almost identical oxygen stoichiometry, $x \approx 0.9$. As a result, the crystal structure of YSCO is tetragonal $P4/mmm$, while the crystal structure of optimally doped YBCO is orthorhombic $Pmmm$, which is expected to alter significantly the electronic structure, as suggested by previous experimental [8], numerical [9] and theoretical [10] studies on the effect of local oxygen ordering in YBCO.

In order to investigate the changes in the electronic structure caused by both the Sr/Ba substitution and the oxygen disorder, we perform the first *ab initio* band structure calculations for the fully doped structure (*i.e.* with $x=1$) of YSCO, both in the ordered and in the disordered cases. Our results show that in YBCO the absence of CuO chains arising from this disorder strongly reduces the density of states (DOS) at the Fermi level E_F, and decreases the doping of the superconducting CuO_2 planes. Due to structural and chemical effects, we find that the same is not true for YSCO.

2. Numerical methods

For the calculations, we use the 'all-electron' full-potential linearised-augmented-plane-waves (FLAPW) method in the local density approximation (LDA) to the density functional theory, as described elsewhere [11, 12]. In the interstitial region we use plane waves with wave vector up to $k_{max} = 3.8$ a.u. and muffin-tin radii: $R_Y = 2.4$ a.u., $R_{Cu} = 1.95$ a.u., $R_{Sr} = 2.8$ a.u., and $R_O = 1.6$ and 1.49 a.u. for the in-plane and apical oxygens, respectively. Inside the muffin-tin spheres, angular momenta up to $l_{max} = 8$ are used to expand potential, charge density and wave functions. The Brillouin zone is sampled using the special k-point technique of the Monkhorst-Pack scheme [13] and also the linear tetrahedron method with up to 125 k-points in the irreducible Brillouin zone to calculate the density of states. The structural parameters of the ordered and disordered YBCO and YSCO equilibrium structures and the relative differences in total energy are computed in the density-functional-theory pseudopotential plane-wave framework. For this calculation we use the VASP code [14, 15] based on ultrasoft pseudopotentials for all the elements involved [16]; Y, Sr and Ba p-semicore states are included in the valence. To treat the exchange-correlation energy functional, we use LDA in the Ceperley-Alder

[17] form parametrised by Perdew and Zunger [18]. We find that LDA gives satisfactory agreement with the experimental (and GGA [19] results, within 1-2%), as shown in Table 1 below. A kinetic energy cutoff of 36 Ry is found to be sufficient to achieve convergence of the electronic and structural parameters. Brillouin zone integration of the formula-unit reciprocal cell is performed on a 8×8×4 Monkhorst-Pack mesh [13]. To ensure energy convergence with respect to k-point sampling, we use an electronic finite-temperature technique with a 0.1 eV Gaussian broadening of the occupation numbers. Atomic positions, cell size and shape are optimised by computing the stresses and the forces with a quasi-Newton algorithm. Convergence of the total energy within 1 meV is achieved by varying the structural parameters.

3. Numerical results

Hereafter, we shall adopt the notation used in Ref. [20] to label the distinct Cu and O sites in the orthorhombic $Pmmm$ symmetry (see Fig. 1), $i.e.$ Cu1 for the copper in the basal plane at (0,0,0), Cu2 for the copper in the CuO_2 plane at (0,0,z), O1 for the apical oxygen at (0,0,z), O2 and O3 for the oxygens in the CuO_2 plane at (1/2,0,z) and (0,1/2,z), respectively, O4 for the chain oxygen at (0,1/2,0) and O5 for the oxygen in the basal plane at (1/2,0,0). Before presenting the results of the calculations, we recall the main features of the band structure of YBCO [21]. There are four partially filled bands at E_F. Two of them arise from the hybridisation of the Cu2(3d)-O2(p)-O3(p) orbitals in the superconducting CuO_2 planes and have two-dimensional character. Their dispersion is strong and nearly symmetric along X-S and Y-S. The other two bands arise from the hybridisation of the Cu1(3d)-O1(p)-O4(p) orbitals in the basal CuO plane and are therefore associated with the CuO chains. The character of these bands is one-dimensional; they are both anti-bonding with respectively σ and π character.

The first issue we address is the purely chemical effect of the isovalent Ba/Sr substitution. To do this, we calculate the band structure of YSCO in the 'frozen' YBCO structure and compare it with that of YBCO (see Figure 2). The close similarity between the two band structures near E_F indicates that the effect is small, but not negligible. The only relevant difference concerns the chain-related π bands (in particular the apical O p_x and Cu d_{xz} states just below E_F at S), which are located at higher energy in YBCO. In conclusion, the larger effect of the Sr substitution is steric, as expected.

We now attempt to understand why in YSCO nature favors the average tetragonal symmetry arising from oxygen disorder in the CuO plane of the orthorhombic symmetry of YBCO. We first minimise the total energy E to determine the unit cell parameters a and b at equilibrium of the hypothetical orthorhombic structure of YSCO with x=1. From Table 1 we see that both the average $\frac{a+b}{2}$ and c are in good agreement with the experimental parameters within less than $\approx$ 2%. To evaluate the reliability of the method, the same calculations are carried out for YBCO as well. From Table 1 we note the same trends and a satisfactory agreement between calculated and experimental parameters for this compound as well. The orthorhombic distortion, expressed by the
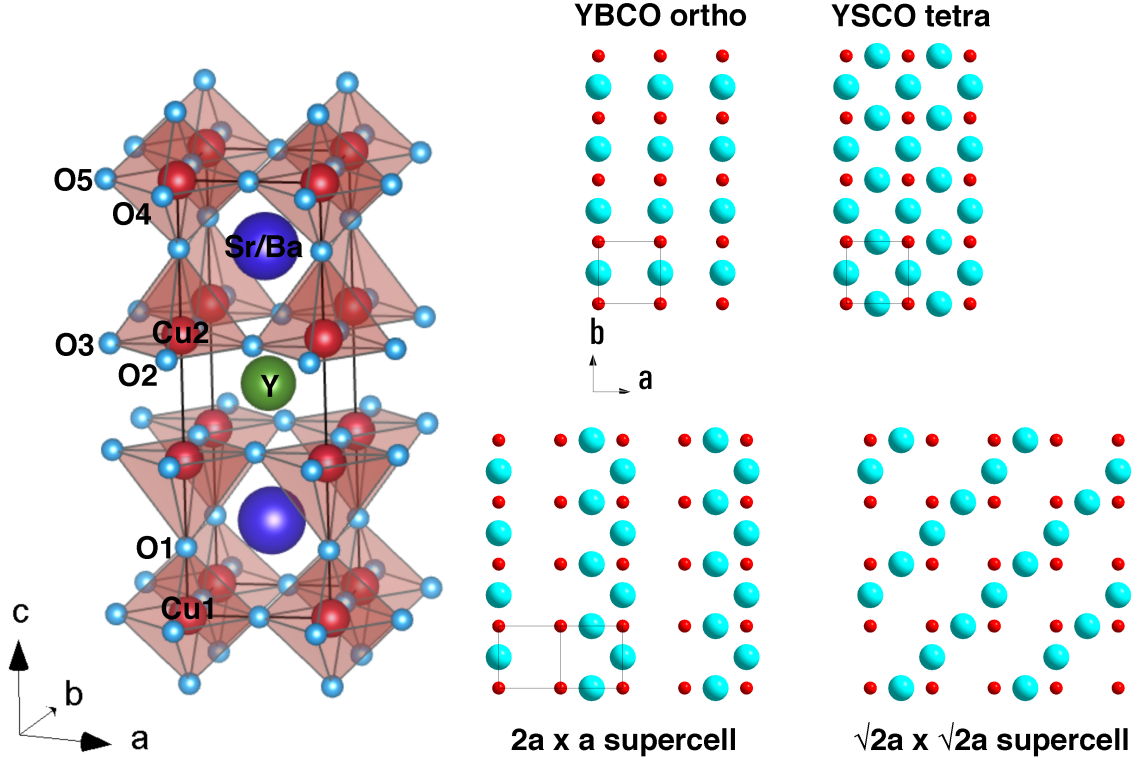
Figure 1. Left: crystal structure of YBCO and of YSCO for $x=1$. Red and light-blue spheres indicate copper and oxygen atoms, respectively. The solid black line indicates the unit cell. The labels of non equivalent Cu and O sites are as described in the text and in Ref. [20]. Note that, in the tetragonal $P4/mmm$ structure of YSCO, the O4 and O5 oxygen sites are partially occupied at 50%, while, in the orthogonal $Pmmm$ structure of YBCO, these two sites are fully occupied and empty, respectively. Right: the following oxygen ordering schemes in the CuO basal planes are shown: (i) orthorhombic YBCO with ordered CuO chains along b; (ii) tetragonal YSCO with equal occupancy of the O4 and O5 sites along the a- and b-directions; (iii) $2a \times a$ and (iv) $\sqrt{2}a \times \sqrt{2}a$ supercells used in the *ab initio* calculations to simulate the absence of CuO chains in the previous case (ii) of tetragonal YSCO.

b/a ratio, is larger in YSCO. Indeed, the smaller Sr cation is more effective in reducing the a parameter, whilst the b parameter is mainly determined by the Cu1-O4 distance.

To investigate how structural relaxation affects the electronic structure of YSCO, we calculate the band structure of the hypothetical orthorhombic structure (with CuO chains), reported in Table 1. The result is shown in Figure 2. We notice the different shape of the chain-related $\pi-$antibonding bands, located near E_F in YBCO and entirely occupied in YSCO. At the S-point, these bands are found at about 0.5 eV below E_F. As a result, the density of states at E_F is reduced to about half of that of YBCO. However, the position of the CuO_2 $d-p_\sigma$ Fermi level crossings is nearly unchanged, implying very similar band fillings in the ordered orthorhombic phase of both compounds.

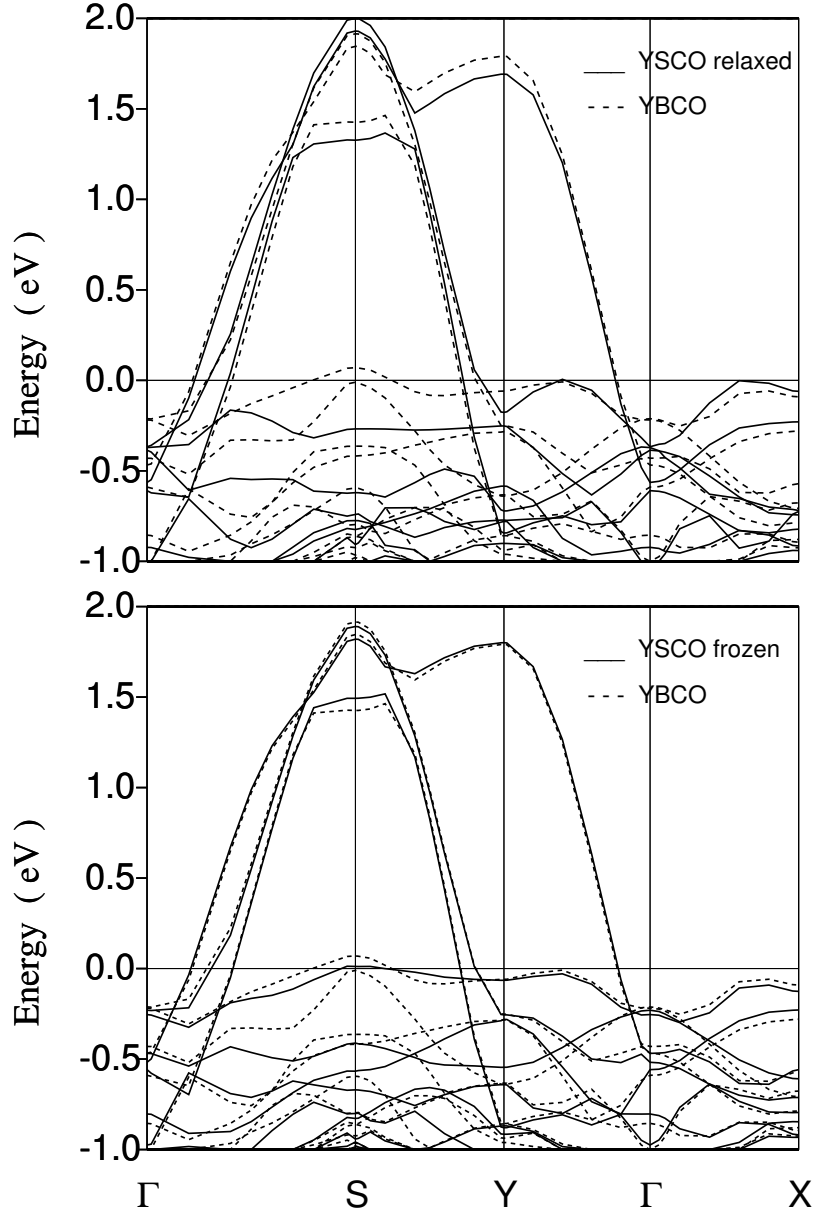The point that remains to be studied is how disorder affects the electronic properties

Figure 2. Lower panel: band structures of YSCO (solid lines) and of YBCO (dashed lines) calculated in both cases using the 'frozen' crystal structure of the latter compound. Upper panel: the same as above using for YSCO the relaxed structure obtained by minimising the total energy.

Table 1. Comparison between experimental and calculated unit cell parameters for ordered and disordered $YSr_2Cu_3O_{6+x}$ (YSCO) and $YBa_2Cu_3O_{6+x}$ (YBCO) in the orthorhombic structure where the CuO chains run along the b-direction. The experimental values labeled as [*] and [†] are taken from Refs. [4] and [22], respectively.

	YSCO			YBCO		
	Exp.[*] (x=1.3)	Calc. (x=1)		Exp.[†] (x=0.9)	Calc. (x=1)	
		ord.	dis.		ord.	dis.
a [Å]	3.79167(15)	3.6596	3.7677	3.8166(3)	3.8057	3.8710
b [Å]	3.79167(15)	3.8025	3.7362	3.8852(3)	3.8604	3.8334
c [Å]	11.4075(11)	11.1732	11.1368	11.6901(9)	11.4642	11.4484
b/a	1	1.039	0.991	1.0168	1.0143	0.990
c/a	3.0078	3.053	2.955	3.0554	3.0123	2.9574

of YSCO. To simulate the oxygen disorder leading to the absence of chains, we assume a realistic local arrangement of the oxygens compatible with the average tetragonal symmetry found experimentally. NQR data [7] give evidence of a random distribution of 1.3 oxygens per unit cell in the two equivalent O4 (0,1/2,0) and O5 (1/2,0,0) positions of the tetragonal symmetry (see Figure 1). To take this random distribution into account with a reasonable computational effort, we consider two different supercells in the ab-plane schematically shown in Figure 1. In both cases the oxygens are ordered in such a way as to avoid almost completely the formation of CuO chains, thus simulating the chain disorder. The first supercell is a primitive orthorhombic, $2a \times a$, with one of the two oxygen atoms in the O4 site in the CuO basal plane shifted to the O5 position. A zig-zag of O atoms is therefore formed along the b axes and one out of two chains is missing. The second supercell is a tetragonal $\sqrt{2}a \times \sqrt{2}a$ (rotated by 45°) with the oxygens ordered along the diagonal ab-direction. No significant orbital overlap (and hence no band formation) is expected to arise from this arrangement, being the O-O distance along this direction as large as 2.68 Å.

For both supercells, we calculate the band structure using the theoretical equilibrium lattice parameters obtained in the pseudopotential approach and reported in Table 1. We recall that these parameters are close to the experimental ones [4, 7]. Since the calculations on both supercells lead to physically similar conclusions, in the following we discuss only the case of the first supercell, for the Brillouin zone folding is simpler in this case. Namely, the single-cell X-point folds into the supercell Γ'-point, while both Y and S of the single cell fold into Y' of the supercell. The X' of the supercell corresponds to the $\Gamma - X$ midpoint, where the folding occurs.

In Figure 3 we compare the supercell result with that of the ordered single-cell phase (*i.e.* with CuO chains) of Figure 2. To do this, we report the single-cell result of Figure 2 folded into the supercell Brillouin zone. We note that the shape of the bands associated with the CuO_2 planes are nearly unchanged by the disorder in

both compounds, as expected since the disorder is located far apart from these planes. Specifically, in $YBa_2Cu_3O_{6+x}$ these bands are nearly rigidly shifted downward in energy in the disordered phase (see, in particular, the region around the Γ and Y' points). This indicates that the disorder leads to a larger filling of the $d-p_\sigma$ bands in YBCO. On the other hand, in $YSr_2Cu_3O_{6+x}$ the disorder does not affect significantly the filling of these bands. A similar situation occurs in $YSr_2Cu_3O_{6+x}$ in the case of the ordered single-cell shown in Figure 2, where the structural relaxation does not appreciably change the $d-p_\sigma$ crossings.

We now focus on the $d_{z^2-y^2}$ σ-bands associated with the CuO chains. From Figure 3 we see for both compounds a strong suppression of the dispersion of the bands. One of these, located at energies ≈ 0.5 eV above E_F and crossing the Fermi level close to the S'-point in YSCO, is nearly flat. The second band is located around 1.2 eV above E_F, at energies ≈ 0.8 eV lower than in the ordered case. The lowering of the empty antibonding bands of the chains (that is even larger in the second supercell, not shown in any figure) implies a less effective binding (lower antibonding band) in the disordered structure, as discussed in detail below. Similar features are found in both compounds by taking into account the oxygen disorder. Nevertheless, in YSCO, unlike in YBCO, a band crosses E_F in the disordered phase near S', while it does not in the ordered phase. Thanks to such disorder-induced band crossing, a hole transfer from the $d_{z^2-y^2}$ σ-band to the $d-p_\sigma$ bands of the superconducting CuO_2 planes is enabled. This tends to compensate the opposite effect of hole depletion induced by the flat $d-p_\pi$ bands.

The above disorder-induced alterations of the electronic structure are observed also in the atomic site projected partial density of states (PDOS) of the first supercell (see Figure 4). The PDOS in the ordered and disordered structures shows sizable differences only for the Cu1, O1 and O4 sites in the basal planes. Namely, the Cu1 and O4 PDOS of the disordered structure reveals a poor hybridisation between O(p) and Cu(3d) orbitals, as also shown by a pronounced peak appearing in the O4 PDOS at $\simeq -5$ eV, a signature of non-bonding state. This is our main result, which suggests charge localisation in the basal planes. As a result, hole transfer from these planes to the CuO_2 planes, the mechanism enabling the metallic (and superconducting) state, is hindered. This scenario is consistent with an earlier model proposed by Burdett [10]. Interestingly, the PDOS result for the Cu2, O2 and O3 sites suggests that the CuO_2 planes are marginally affected by the fragmentation of the CuO chains.

4. Discussion

We try to understand why oxygen disorder is favored in YSCO by computing the free energy F in the ordered and in the disordered phase of both YSCO and YBCO. We first compare the total energy E contributions. As before, the disorder is simulated by the previous two supercells. Our calculations indicate that the differences of total energy between disordered and ordered structures are similar in YBCO and in YSCO. For both compounds, we obtain a difference $\Delta E \approx 0.5$ eV/supercell in excellent agreement
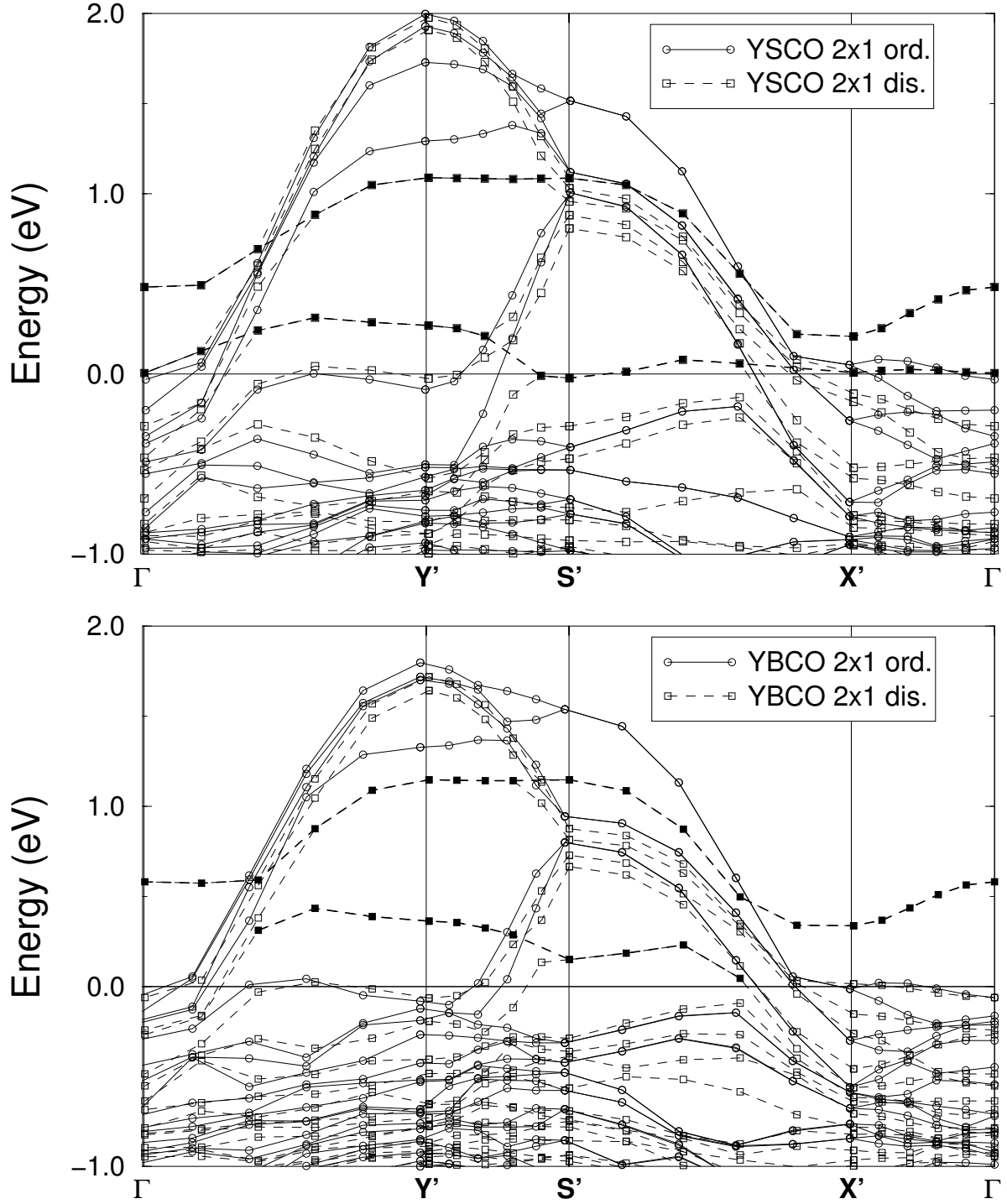
Figure 3. Band structures of YSCO and YBCO calculated for the ordered and disordered $(2a \times a)$ structures of Figure 1. Black dashed lines with full symbols highlight bands related to $d_{z^2-y^2} - \sigma$ bands coming from Cu-O chains. As no symmetry analysis has been included, lines are only a guide to the eye.
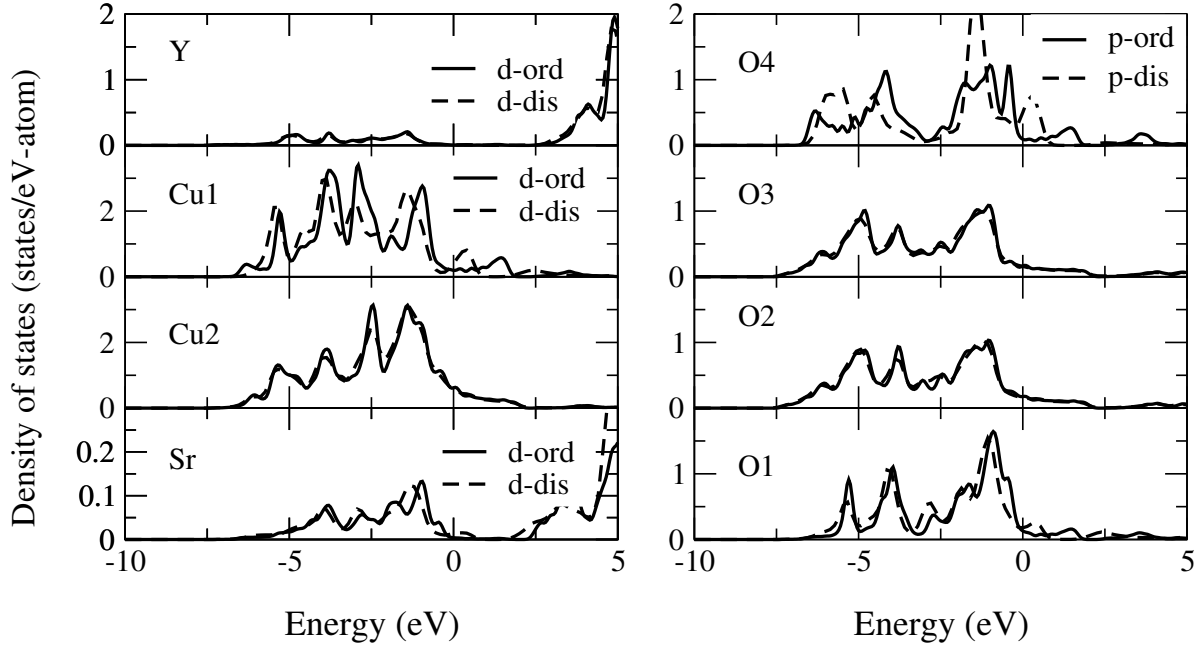
Figure 4. Projected density of states (PDOS) of the YSCO ordered and disordered $(2a \times a)$ supercell structures of Figure 1. Site labels are defined in the text. Note the appearance of a pronounced peak at $\simeq -0.5$ eV in the O4 PDOS of the disordered structure.

with the value of 0.46 eV obtained from Monte Carlo simulations [23, 24, 25]. Thus, the driving force of disorder in YSCO does not arise from total energy differences. We then evaluate the entropy contribution made of the electronic, configurational and phononic terms. The latter term can not be easily calculated, especially in disordered structures. Though, in first approximation, we may neglect this term considering that the lattice dynamics in the ordered and disordered phases should not differ significantly from YBCO to YSCO. This is indeed a reasonable assumption considering that the relevant quantity entering the entropy expression is the phononic DOS and previous neutron scattering [26] and specific heat [27] studies show that this quantity does not change appreciably in YBCO upon substituting Y with a heavier rare earth element. This result is not surprising considering that the isovalent chemical substitution of only one of the 13 atoms forming the unit cell will affect only a limited number of phonon modes. A similar situation should then occur in the present case of Sr/Ba substitution.

We then estimate the remaining two terms. As for the electronic term, we recall that, in YBCO, the disruption of the chain-related $\pi-$antibonding bands reduce $N(E_F)$ and, consequently, the electronic entropy. We conclude that, in YBCO, the electronic entropy tends to stabilise the ordered phase with long chains. The opposite conclusion is drawn for YSCO for two reasons. 1) The π band is located below E_F, independent of the ordering; 2) the disorder lowers a chain-related $d_{z^2-y^2}$ $\sigma-$antibonding band, located *above* E_F in the ordered phase. At the S'-point, this band even crosses E_F, thus enhancing $N(E_F)$ and the entropic term favorable to the disordered phase.

Quantitatively, we estimate the above differences by computing the difference $\Delta S \equiv S_{dis} - S_{ord}$ between ordered and disordered phases using the usual expression

$$S_{el}^{(dis,ord)} = -k_B \int N^{(dis,ord)}(\varepsilon)[f(\varepsilon) \ln f(\varepsilon) + (1 - f(\varepsilon)) \ln(1 - f(\varepsilon)]\gamma \, d\varepsilon$$

where $\gamma \equiv m^*/m$ is the effective mass enhancement factor for the electron, k_B is the Boltzmann constant, $f(\varepsilon)$ is the Fermi-Dirac distribution function and the density of states $N(E_F)$ is obtained from accurate fits of the energy bands. The above expression must be evaluated at the temperature $T = 1323$ K at which the YSCO samples are synthesised and subsequently quenched down to room temperature [4]. For YBCO, we obtain a *negative* entropic contribution to the free energy $T\Delta S_{el} \approx -0.07\gamma$ eV/supercell. By using the experimental $\gamma = 5$ value reported for fully doped YBCO [28], we obtain a contribution of comparable magnitude, but with opposite sign, with respect to the positive difference of configurational entropy $T\Delta S_{conf} = 2k_B T \ln(2) = 0.158$ eV. In conclusion, in YBCO, the algebraic sum of both contributions to $T\Delta S$ is estimated to be smaller than the total energy difference. This conclusion is in agreement with the stability of the orthorhombic phase of YBCO found experimentally. On the contrary, in YSCO, we estimate a *positive* electronic contribution $T\Delta S_{el} \approx 0.04\gamma$ eV. Consequently, the sum of configurational and electronic contributions to the entropic term TS is positive and sizeable. By assuming again $\gamma = 5$, we obtain $T\Delta S_{el+conf} \approx 0.36$ eV. The latter value clearly indicates that the disorder is more favored in YSCO than in YBCO but the corresponding free-energy gain is still smaller than the relevant energy difference. Therefore our calculations would fully account for the disorder in stoichiometric YSCO only in the case of higher $\gamma \approx 8-10$ values, as reported in Ref.[29, 30], or if the phononic contribution would play an important role.

A key to elucidate this point may be provided by a high-resolution transmission electron microscopy study on both over- ($x = 1.3$) and under-stoichiometric ($x = 0.9$) compounds [6]. This study shows that the former compounds, with 0.3 excess oxygens per unit cell with respect to the stoichiometric phase [3, 4], exhibit no trace of oxygen ordering in the local scale. On the contrary, the latter compounds mainly consist of a modulated phase with $4a$-long CuO chain fragments. We conclude that oxygen overdoping is likely to favor the disordered phase. In turn, T_c increases by only 4-5 K upon reducing x from 1.3 to 0.9, which indicates that the as-prepared samples are overdoped and that the maximum T_c is intrinsically smaller in YSCO than in YBCO.

5. Conclusions

In conclusion, we have studied the effects of oxygen disorder on the electronic structure of stoichiometric $YSr_2Cu_3O_{6+x}$ (*i.e.* for $x=1$) by calculating the *ab initio* band structure of two tetragonal supercells simulating disordered CuO chains and of an hypothetical orthorhombic structure with ordered CuO chains, isostructural to that of stoichiometric $YBa_2Cu_3O_{6+x}$. For comparison, we carried out the same calculations on the latter phase as well. In agreement with experiments, we find that the orthorhombic ordered

phase, where CuO chains are formed along the b-axis direction, is thermodynamically favored in $YBa_2Cu_3O_{6+x}$. In $YSr_2Cu_3O_{6+x}$, we find an incipient oxygen disorder that may be stabilised by oxygen overdoping, as suggested by the experimental evidence of average tetragonal symmetry and by the absence of any oxygen ordering in the local scale reported for samples with $x = 1.3$. This phenomenon provides a hint to explain the 30 K reduction of T_c in YSCO with respect to YBCO and raises the question whether a similar situation may contribute to the large T_c variations observed in cuprates.

Acknowledgments

References

[1] Bednorz J G and Müller K A 1986 *Zeitschrift für Physik B Condensed Matter* **64** 189–193 ISSN 1431-584X URL https://doi.org/10.1007/BF01303701

[2] Okai B 1990 *Japanese Journal of Applied Physics* **29** L2193 URL http://stacks.iop.org/1347-4065/29/i=12A/a=L2193

[3] Cao Y, Hudson T L, Wang Y S, Xu S H, Xue Y Y and Chu C W 1998 *Phys. Rev. B* **58**(17) 11201–11203 URL https://link.aps.org/doi/10.1103/PhysRevB.58.11201

[4] Gilioli E, Radaelli P, Gauzzi A, Licci F and Marezio M 2000 *Physica C: Superconductivity* **341-348** 605 – 606 ISSN 0921-4534 materials and Mechanisms of Superconductivity High Temperature Superconductors VI URL http://www.sciencedirect.com/science/article/pii/S0921453400006109

[5] Gauzzi A, Gilioli E, Licci F, Marezio M, Massidda S, Bernardini F, Continenza A and Radaelli P G 2000 *Proc. SPIE* **4058** 4058 – 4058

[6] Lebedev O I, Van Tendeloo G, Licci F, Gilioli E, Gauzzi A, Prodi A and Marezio M 2002 *Phys. Rev. B* **66**(13) 132510 URL https://link.aps.org/doi/10.1103/PhysRevB.66.132510

[7] Prodi A, Gauzzi A, Gilioli E, Licci F, Marezio M, Bolzoni F, Allodi G, De Renzi R, Bernardini F, Massidda S, Profeta G, Continenza A and Radaelli P G 2003 *International Journal of Modern Physics B* **17** 873–878 (*Preprint* https://doi.org/10.1142/S0217979203016753) URL https://doi.org/10.1142/S0217979203016753

[8] Jorgensen J, Pei S, Lightfoor P, Shi H, Paulikas A and Veal B 1990 *Physica C: Superconductivity* **167** 571 – 578 ISSN 0921-4534 URL http://www.sciencedirect.com/science/article/pii/0921453490906766

[9] Poulsen H F, Andersen N H, Andersen J V, Bohr H and Mouritsen O G 1991 *Phys. Rev. Lett.* **66**(4) 465–468 URL https://link.aps.org/doi/10.1103/PhysRevLett.66.465

[10] Burdett J K 1992 *Physica C: Superconductivity* **191** 282 – 291 ISSN 0921-4534 URL http://www.sciencedirect.com/science/article/pii/0921453492906605

[11] Jansen H J F and Freeman A J 1984 *Phys. Rev. B* **30**(2) 561–569 URL https://link.aps.org/doi/10.1103/PhysRevB.30.561

[12] Wimmer E, Krakauer H, Weinert M and Freeman A J 1981 *Phys. Rev. B* **24**(2) 864–875 URL https://link.aps.org/doi/10.1103/PhysRevB.24.864

[13] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13**(12) 5188–5192 URL https://link.aps.org/doi/10.1103/PhysRevB.13.5188

[14] Kresse G and Hafner J 1993 *Phys. Rev. B* **47**(1) 558–561 URL https://link.aps.org/doi/10.1103/PhysRevB.47.558

[15] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54**(16) 11169–11186 URL https://link.aps.org/doi/10.1103/PhysRevB.54.11169

[16] Vanderbilt D 1990 *Phys. Rev. B* **41**(11) 7892–7895 URL https://link.aps.org/doi/10.1103/PhysRevB.41.7892

[17] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45**(7) 566–569 URL https://link.aps.org/doi/10.1103/PhysRevLett.45.566

[18] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23**(10) 5048–5079 URL https://link.aps.org/doi/10.1103/PhysRevB.23.5048

[19] Long R and Prezhdo O V 2017 *The Journal of Physical Chemistry Letters* **8** 193–198 URL https://doi.org/10.1021/acs.jpclett.6b02713

[20] Capponi J J, Chaillout C, Hewat A W, Lejay P, Marezio M, Nguyen N, Raveau B, Soubeyroux J L, Tholence J L and Tournier R 1987 *EPL (Europhysics Letters)* **3** 1301 URL http://stacks.iop.org/0295-5075/3/i=12/a=009

[21] Yu J, Massidda S, Freeman A and Koeling D 1987 *Physics Letters A* **122** 203 – 208 ISSN 0375-9601 URL http://www.sciencedirect.com/science/article/pii/0375960187908073

[22] Simon A, Köhler J, Borrmann H, Gegenheimer B and Kremer R 1988 *Journal of Solid State Chemistry* **77** 200 – 203 ISSN 0022-4596 URL http://www.sciencedirect.com/science/article/pii/0022459688901107

[23] Mønster D, Lindgård P A and Andersen N H 1999 *Phys. Rev. B* **60**(1) 110–113 URL https://link.aps.org/doi/10.1103/PhysRevB.60.110

[24] Mannstaedt S and Pawley G S 2000 *Phys. Rev. B* **62**(6) 4169–4174 URL https://link.aps.org/doi/10.1103/PhysRevB.62.4169

[25] Mønster D, Lindgård P A and Andersen N H 2001 *Phys. Rev. B* **64**(22) 224520 URL https://link.aps.org/doi/10.1103/PhysRevB.64.224520

[26] Renker B, Gompf F, Gering E, Roth G, Reichardt W, Ewert D and Rietschel H 1988 *Physica C: Superconductivity* **153-155** 272 – 273 ISSN 0921-4534 URL http://www.sciencedirect.com/science/article/pii/0921453488905886

[27] Meulen H V D, Franse J, Tarnawski Z, Kadowaki K, Klaasse J and Menovsky A 1988 *Physica C: Superconductivity* **152** 65 – 71 ISSN 0921-4534 URL http://www.sciencedirect.com/science/article/pii/0921453488900731

[28] Fiory A T, Hebard A F, Eick R H, Mankiewich P M, Howard R E and O'Malley M L 1990 *Phys. Rev. Lett.* **65**(27) 3441–3444 URL https://link.aps.org/doi/10.1103/PhysRevLett.65.3441

[29] Yeh N C and Tsuei C C 1989 *Phys. Rev. B* **39**(13) 9708–9711 URL https://link.aps.org/doi/10.1103/PhysRevB.39.9708

[30] Hopfengärtner R, Leghissa M, Kreiselmeyer G, Holzapfel B, Schmitt P and Saemann-Ischenko G 1993 *Phys. Rev. B* **47**(10) 5992–6003 URL https://link.aps.org/doi/10.1103/PhysRevB.47.5992