Electronic structure and energetics of tetragonal $SrCuO_2$ and its high-pressure superstructure phase

2011 J. Phys.: Condens. Matter 23 465503

(http://iopscience.iop.org/0953-8984/23/46/465503)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **23** (2011) 465503 (6pp) doi:10.1088/0953-8984/23/46/465503

Electronic structure and energetics of tetragonal $SrCuO_2$ and its high-pressure superstructure phase

Jianwei Wang[1], **Zsolt Rak, Fuxiang Zhang, Rodney C Ewing and Udo Becker**

Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA

E-mail: jwwang@umich.edu

Received 18 July 2011, in final form 6 October 2011
Published 4 November 2011
Online at stacks.iop.org/JPhysCM/23/465503

Abstract

First-principles calculations have been used to investigate the electronic structure and energetics of the simple tetragonal $SrCuO_2$ ($P4/mmm$) and its high-pressure tetragonal superstructure ($P4/mmm$). Based on the calculations, the high-pressure phase is metastable as compared with the low pressure tetragonal phase, with an energy difference of 0.13 eV per $SrCuO_2$ formula unit. The energy barrier to the transition from the superstructure to the simple tetragonal structure is 0.24 eV at 7 GPa; thus, high temperatures are required to synthesize the latter. Among the possible structural configurations resulting from the partially occupied oxygen site in the superstructure phase, the most stable structure has a space group $P\bar{4}m2$, reduced from that of the simple tetragonal structure $P4/mmm$. The detailed analysis of the electronic band structures of the simple tetragonal and superstructure phases suggests that the out-of-plane buckling of the O atoms in the superstructure leads to significant decrease in the O p–Cu d orbital overlap, allowing the energy of the system to be lowered, which is necessary for the structural stability. An understanding of the electronic structure and energetics of the high-pressure superstructure phase and its relation to the simple tetragonal phase provides a basis for exploring the physical properties of the infinite layer, high-T_C superconductor.

(Some figures may appear in colour only in the online journal)

1. Introduction

The tetragonal cuprate, $SrCuO_2$, and its doped compounds have been a subject of extensive studies [1–7]. The structure is two-dimensional and becomes a high-temperature superconductor upon hole-doping [8, 9]. The tetragonal $SrCuO_2$ has a simple structure with infinite, two-dimensional CuO_2 planes separated by layers of Sr atoms [10]. The synthesis of this simple tetragonal phase, however, is not straightforward because it is metastable at ambient conditions. The stable phase is orthorhombic and the transition to the tetragonal phase in undoped as well as for most doped compositions of $SrCuO_2$ can be achieved at high pressure and high temperature [10]. Recently, at room temperature and pressures above 7 GPa, a new tetragonal superstructure phase has been observed for the pure $SrCuO_2$. The new structure results from the splitting of one O site along the *c*-axis [1]. This superstructure cannot be quenched at ambient temperature and pressure, and it reversibly transforms to the orthorhombic phase. It remains to be understood why temperature treatment is required at high pressure in order to synthesize the simple tetragonal phase from the orthorhombic phase.

At room temperature and high pressure the orthorhombic phase transforms to the tetragonal superstructure, while at high temperature and high pressure it transforms to the simple, infinite-layer tetragonal phase. Temperature may provide the necessary activation energy to the system such that the transition from the superstructure to the simple tetragonal structure may occur. It is expected that the structural,

---

[1] Author to whom any correspondence should be addressed.

energetic, and electronic relations between the tetragonal and superstructure phases would provide important clues about the phase transition and stabilities. A fundamental understanding of the phase relations is important for the synthesis and design of the compound. In addition, most physical properties of the high-pressure tetragonal $SrCuO_2$ superstructure have not been investigated. It has not been determined whether a doped $SrCuO_2$ tetragonal superstructure exists and whether it is a high-temperature superconductor.

In this study, first-principles electronic structure calculations were completed on both the high-pressure superstructure and the simple tetragonal phases, with the aim of achieving a fundamental understanding of the energetics of both structures. In order to see whether high-temperature treatment provides the necessary activation energy to stabilize the simpler tetragonal phase, *ab initio* calculations were performed to calculate the energy difference of the two phases, as well as the energy barriers of the transition from the tetragonal superstructure to the simple tetragonal phases at different pressures. The electronic origin of this transition was examined by comparing the calculated electronic band structures of $SrCuO_2$ in the two configurations. Possible local ordering of the tetragonal superstructure phase is discussed in the light of the calculated energetics.

2. Methods

The first-principles calculations were carried out using two different methods within density functional theory (DFT). In order to calculate and compare the energetics of the simple tetragonal (figure 1(a)) and the superstructure phases (figure 1(b)), the pseudopotential method in combination with the B3LYP hybrid functional was used [11], as implemented in the CRYSTAL package [12]. The B3LYP functional has been successfully applied to many periodic systems, including $CaCuO_2$, since it has enough variational freedom to describe 3d electron systems [2]. In addition, to examine details of the electronic band structures of $SrCuO_2$ in the two structural configurations, the full-potential linearized augmented plane wave method (FP-LAPW) was used [13], as implemented in the WIEN2k package [14].

To investigate the energetics of the transition between the two phases, unit cells with 4 $SrCuO_2$ units (16 atoms) were examined. The setup of the computational parameters for the $SrCuO_2$ was similar to the one presented in [2] (for $CaCuO_2$) except that for the Sr ion, a small-core Hay–Wadt pseudopotential in the form of 31(3d)G was used [15]. The all-electron basis sets for Cu and O ions were of the forms 86-4111(41d)G [16] and 8-411G [17], respectively. The optimization of the simple tetragonal structure was tested for k-points and convergence tolerance. 75 k-points in the irreducible part of the Brillouin zone (IBZ) were used. With regard to the spin configuration of the Cu ions, the antiferromagnetic (AFM) arrangement is energetically more favorable by 0.273 eV per unit cell as compared with the ferromagnetic (FM) case. As shown in a previous study [2], the two-dimensional and three-dimensional AFM spin structures have similar energies since the interaction between the layers is weak. Thus, for simplicity, the two-dimension AFM structure, where spins on Cu are antiferromagnetic only within the Cu–O layer, was used as the initial constraint throughout the calculations (figure 1(a)).

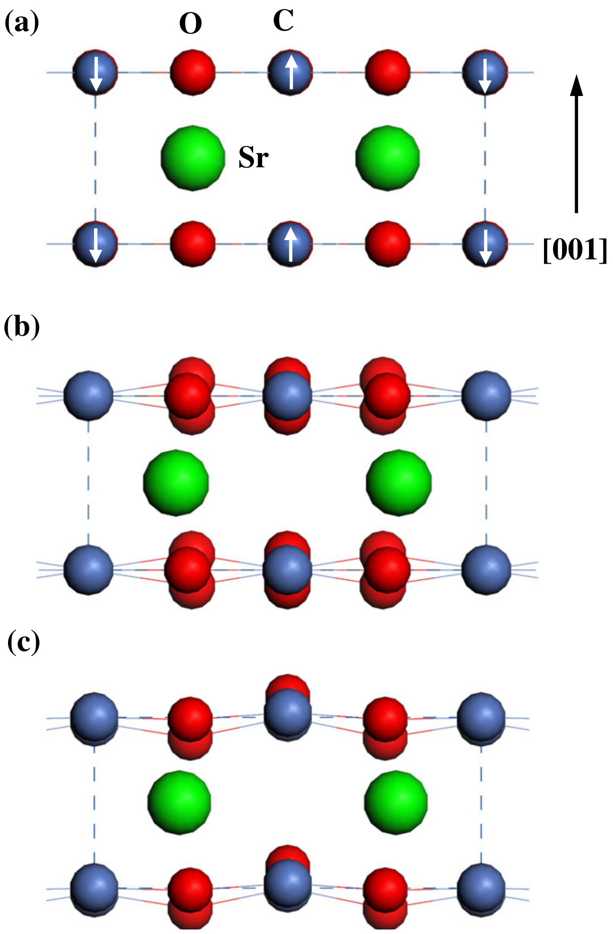

Figure 1. Structures of $SrCuO_2$: (a) the simple tetragonal structure represented in a $2 \times 2 \times 1$ supercell, (b) the disordered superlattice structure, and (c) the calculated tetragonal superlattice structure. The green balls are Sr ions, the blue balls are Cu ions, and the red balls are O atoms. The thick blue dashed lines represent the computational or crystallographic unit cell. The thin lines are bonds between Cu and O.

The simple tetragonal phase (figure 1(a)) has a space group $P4/mmm$ and cell parameters $a = b = 3.952(2)$ Å and $c = 3.389(2)$ Å [18], while the dimensions of the superstructure (also $P4/mmm$, figure 1(b)) are doubled in the crystallographic a and b directions ($2a \times 2b \times c$) [1]. For consistency in the total energy calculations and in the dimensions of the computational models, the simple tetragonal phase was modeled with a $2\times2\times1$ supercell, where the unit cell parameters are doubled along the a and b axes.

The calculations of the electronic energy bands were completed using the highly accurate FP-LAPW method, in combination with the generalized gradient approximation (PBE-GGA) [19] for the exchange–correlation potential. In order to handle the strong intra-atomic Coulomb interaction within the Cu d shell, an orbital dependent potential (GGA + U) was included in the calculations, in the form introduced by Anisomov *et al* in 1993 [20], with an approximate correction for self-interaction. This functional is often mentioned in the literature as the fully localized limit (FLL) [21]. The inclusion of this electronic correlation (Hubbard U) is necessary in order to reproduce the insulating ground state of the infinite-layer $SrCuO_2$. Calculations were completed for several different values of U ($U = 3.5$, 5.0, 7.5 and 9.0 eV), and the minimum required value for obtaining a semiconducting state was $U = 7.5$ eV. Therefore, this value was used for the band structure calculations.

In order to compare the electronic energy bands of the simple tetragonal $SrCuO_2$ with the superstructure phase, the high-pressure superstructure phase was modeled by using a small unit cell (one Sr, one Cu, and two O atoms) with the two oxygen atoms moved out of the CuO_2 plane (one above and one below the CuO_2 plane). In this way, the effect of 'out-of-plane' buckling of the O atoms on the electronic structure of $SrCuO_2$ could be examined. Furthermore, by choosing this small cell, complications arising from Brillouin-zone (BZ) folding associated with a supercell calculation could be avoided, which would make the comparison between the band structures quite cumbersome.

3. Results and discussion

3.1. Structure of the high-pressure tetragonal phase

The optimized cell parameters for both the phases were approximately 2% larger than the experimental values [1, 18], a difference that is typical of DFT–GGA calculations. In order to reproduce the two-dimensional AFM configuration, no symmetry constraints were imposed on the system, and this spin configuration (figure 1(a)) remained stable after the ionic and electronic optimizations. In the case of the simple tetragonal system, the calculated magnetic moment of the Cu ion was 0.59 μ_B, which is in reasonably good agreement with 0.51 μ_B, measured for the $CaCuO_2$ phase [2] in neutron scattering experiments [22]. These results suggest that the computational method based on the B3LYP functional, employed here, is adequate for describing the crystal structure and electronic structure of the phases and should also be suitable to reasonably understand the energetics of the phase transition between the simple tetragonal and the tetragonal superstructure phases of $SrCuO_2$.

Based on the x-ray diffraction (XRD) data, the superstructure has two O sites: 4l and 8t. The 8t site has 1/2 occupancy, and its coordinates are shifted up from the Cu plane along the *c*-axis (by 0.3 Å at 11.2 GPa) [1]. In the computational model, several different configurations were considered by removing half of the O atoms at the 8t site in the supercell. The structure with lowest energy was found to belong to the space group $P\bar{4}m2$ (no. 115), which is a subgroup of $P4/mmm$ (no. 123), the simple tetragonal phase. This structure was chosen as model for the high-pressure tetragonal superlattice phase (figure 1(c)). The calculated x-ray diffraction pattern using this ordered model was similar to that of the disordered model, derived from the observed x-ray diffraction (XRD) data [1]. However, it is difficult to differentiate the disordered and ordered models solely based on the XRD data. This is largely because the difference between the two models only depends on the positions of the oxygen atoms on one site, and the XRD signal from the oxygen atoms is overshadowed by much the heavier elements Sr and Cu in the structure. The agreement between the measured XRD pattern and the calculated one, based on the ordered model, suggests that the calculated structure is an adequate model for the superstructure phase. In going from the simple tetragonal structure to the high-pressure superstructure phase, the four-fold symmetry at the Cu site is reduced to four-fold inversion symmetry. The other symmetry elements do not change from one phase to the other.

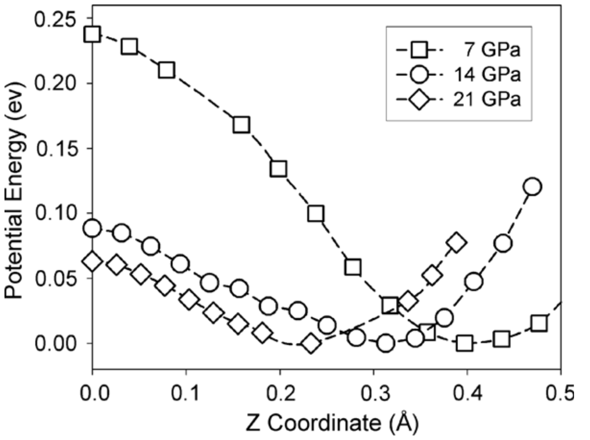

Figure 2. Potential energy surfaces of the O atom along the splitting direction at different pressures. The dashed lines are guides to the eye. The square, circle, and diamond symbols are calculations at different pressures of 7 GPa, 14 GPa, and 21 GPa, respectively.

3.2. Energetics of the high-pressure tetragonal superstructure

The energy barrier for the transition from the superlattice structure to the simple tetragonal phase was estimated by moving one of the O atoms at the 8t site along the normal to the Cu–O_2 plane, in steps of 0.02 Å, from an out-of-plane position toward the Cu–O_2 plane. This method of calculating the energetics through a transition path is similar to the well known nudged elastic band (NEB) method [23]. In the total energy calculations, a constraint on the system was imposed, namely the positions of all Sr ions were kept fixed at their optimized positions. Without such a constraint, the system would spontaneously change to the relaxed superlattice structure. However, by constraining the Sr positions artificially, the calculated path may be altered from the physical path with possible relaxations involving Sr atoms, resulting in errors of the calculated structure and overestimation of the calculated energy barriers. The calculated potential energy values at different pressures are shown in figure 2, where the horizontal axis represents the splitting of the O atom from the Cu–O_2 plane. The potential energy minima were obtained for oxygen splitting distances of ~0.4, 0.3, and 0.2 Å at pressures of 7, 14, and 21 GPa respectively. The experimental value is 0.3 Å at 11.2 GPa [1], which is the value calculated at 14 GPa. A

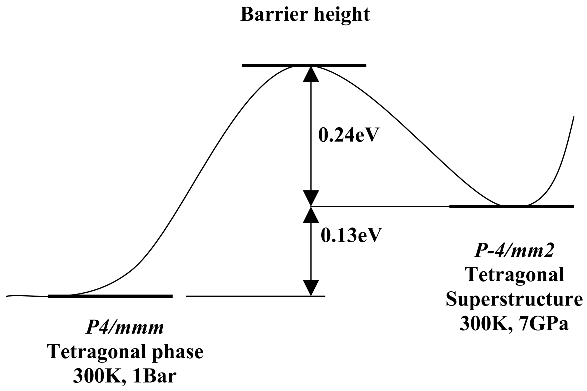

Figure 3. Energetic and phase relationship between the superstructure and the tetragonal structure.

small difference (∼3 GPa) in calculated pressure for the same O-splitting reflects the error in the calculated structure, which originates from the methods used in this study, including the position constraints used in the barrier calculations. The small difference in pressure indicates that the constraint of fixing the positions of the Sr atoms does not significantly affect qualitative understanding and correct prediction of the crystal structure at high pressure. The energy barriers, which have to be overcome in order for the transition from one phase to another to take place, are 0.24, 0.09, and 0.06 eV at pressures of 7, 14, and 21 GPa, respectively. By moving the O atoms into the Cu plane and relaxing all the atoms in the computational cell, the simple tetragonal structure is recovered and the energy is reduced by 0.13 eV (at 7 GPa). This result confirms that the tetragonal superstructure is metastable with respect to the simple tetragonal $SrCuO_2$ phase at high pressure.

Figure 3 shows a schematic of the energetics between the two tetragonal phases. The barrier at 7 GPa is 0.24 eV, much greater than $k_B T$ (0.0256 eV) at room temperature. Although the tetragonal phase with a simple structure is lower in energy by 0.13 eV, and more stable than the superstructure, the energy barrier is too high for the phase transition to occur at room temperature. The high-temperature treatment, often at 1000 K and 6 GPa [10], which is required to synthesize the simple tetragonal phase, probably serves the purpose of providing enough kinetic energy for the system to overcome the barrier of the phase transition. Based on the calculated energy barrier at 7 GPa, the fraction of the split O atoms at the top of the transition barrier is ∼6% at 1000 K, as calculated from the Boltzmann factor. This fraction of split O atoms may be required for the phase transition to occur at 6 GPa and 1000 K [10]. Although the absolute values of the calculated energetic barriers could be overestimated because of the constraints applied in the calculations, the dependence of the energy barrier on pressure is expected to be more reliable and suggests that as pressure increases the required temperature for the phase transition is lower.

Based on the x-ray diffraction result [1], the 8t site is partially occupied with O atoms, indicating a long-range disorder. The calculated ordered structure shows a possible ordering of O atoms around Cu atoms in the superstructure phase. Such ordering could be short-range and may not be detected by x-ray diffraction. If the oxygen atoms have long-range disorder, such long-range disorder is expected to be static at room temperature because the calculated energy barrier against moving an oxygen atom from one side of the Cu plane to the other is 0.24 eV. This value is approximately 10 times greater than the room temperature thermal energy, $k_B T$.

3.3. Electronic structure

The theoretical investigation of the electronic properties of the infinite-layer cuprates ($CaCuO_2$ and $SrCuO_2$) is quite interesting, as they are parent compounds for the high-T_C superconductors, and they have a very simple crystal structure and small unit cell. The undoped systems contain only four atoms per unit cell, with the CuO_2 planes separated by single atomic layers of Ca or Sr. Consequently, there are quite a few theoretical studies investigating the structural, dynamical, and electronic properties of $CaCuO_2$ and $SrCuO_2$ systems [2, 24–32]. The electronic structure of $Ca_{1-x}Sr_xCuO_2$ compounds exhibits very little dependence on the x value. However, since many of these studies are based on the standard local (spin) density approximation (L(S)DA), they fail to describe the correct insulating ground state of the cuprate systems, due to the lack of intra-atomic Coulomb correlation inherent in the L(S)DA functional. In order to overcome this deficiency, one has to go beyond standard DFT–L(S)DA and include an orbital dependent potential in the calculation, to account for the strong Coulomb repulsion within the localized Cu d orbitals [25, 32]. Hybrid methods, based on the B3LYP density functional, as used in this paper for the energetics of the phase transition, also capture the physics of strongly correlated systems and generate the correct ground state electronic structure for the infinite-layer cuprates [2, 30].

The electronic structure of the simple tetragonal $SrCuO_2$ was investigated, and compared with the high-pressure superstructure phase. As mentioned in section section 3.2, for the electronic structure calculations, the high-pressure superstructure was modeled by a small unit cell, containing two O atoms, one Sr atom, and one Cu atom, with the O atoms shifted above and below the Cu plane. Clearly, this simple model does not allow for AFM spin configuration. However, since we are only interested in the electronic origin of the ‘out-of-plane’ buckling of O atoms, the ferromagnetic (FM) setup serves the purpose.

The electronic density of states (DOS) projected on the Cu 3d and O 2p orbitals is shown in figure 4. For both the simple tetragonal and high-pressure structures, the main Cu 3d weight is below −5 eV, while the bands closer to the Fermi energy (E_F) are mainly of O 2p character with small Cu 3d admixture. In the high-pressure phase, the DOSs associated with the Cu 3d orbitals are slightly wider, indicating a somewhat stronger hybridization with other valence band (VB) states, as compared to the simple tetragonal phase.

The electronic band structures of $SrCuO_2$ in the simple tetragonal and high-pressure phases are shown in figure 5. Both spin-up (figures 5(a), (c)) and spin-down (figures 5(b), (d)) channels are represented. In general, the overall shapes

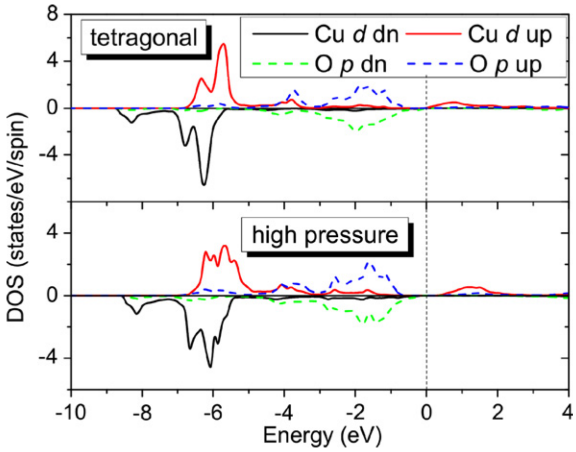

Figure 4. Electronic density of states projected onto Cu 3d and O 2p orbitals in the simple tetragonal (upper panel) and high-pressure (lower panel) phases. The spin-up states are represented on the positive axis while the spin-down states are shown with negative values.

and dispersions of the electronic bands are similar as one goes from the simple, infinite-layer structure (figures 5(a), (b)) to the high-pressure phase (figures 5(c), (d)). The VB and the bottom of the conduction band (CB) are composed mainly of hybridized Cu 3d and O 2p orbitals. The bands along the Γ–Z direction are quite flat, indicating that the interaction between the atomic layers (CuO_2) is rather weak. This is consistent with previous theoretical calculations [2] and experimental results [33], according to which the interlayer magnetic coupling is about two orders of magnitude weaker than the intralayer coupling. The only bands that show some dispersion along the Γ–Z direction are the O p_z bands. This is because the O p_z orbitals are the ones facing the interlayer region.

In order to understand the electronic origin of the high-pressure phase, the details of the electronic bands in the vicinity of E_F were examined and the main differences between the two phases were analyzed. The out-of-plane buckling of the O atoms mainly alters the overlap and hybridization between the O p and Cu d orbitals. Therefore, the way in which the band (orbital) ordering changes from the simple tetragonal to the high-pressure phase needs to be examined. One of the most noticeable differences between the two band structures is found at the top of the VB at the A-point, where the uppermost VB shifts below the lower-lying band when the O atom is moved out of the Cu plane (figures 5(b) and (d)). In the simple tetragonal phase, the top of the VB at the A-point is a linear combination (antibonding state with σ-character) of the O p_y and Cu $d_{x^2-y^2}$ orbitals. When the O atoms are shifted out of the Cu plane, the degree of p_y–$d_{x^2-y^2}$ mixing decreases and the O p_y orbitals will rather hybridize with Cu d_{xy}, giving rise to an antibonding state with π-character. This leads to significant decrease in the O p–Cu d orbital overlap and consequently the uppermost VB at the A-point moves below the lower-lying band (which has O p_x character), allowing the energy of the system to be lowered. A similar line of reasoning can be applied for the top valence bands at the X–point. In the simple tetragonal configuration (figures 5(a) and (b)), the two uppermost bands correspond to the antibonding combinations of the O p_z–Cu d_{xz+yz} orbitals and O p_x–Cu d_{xy} orbitals. They both have π-bond character. When the O atom is moved out of the Cu plane, the overlap between the O p_z and Cu d_{xz+yz} orbitals decreases faster than the O p_x and Cu d_{xy} overlap. Therefore, the top of the p_z–d_{xz+yz} band shifts below the p_x–d_{xy} band, leading to the decrease of the energy. Exactly the same argument is applicable to the ordering of the lower-lying valence bands at the A-point, as indicated in figure 5.

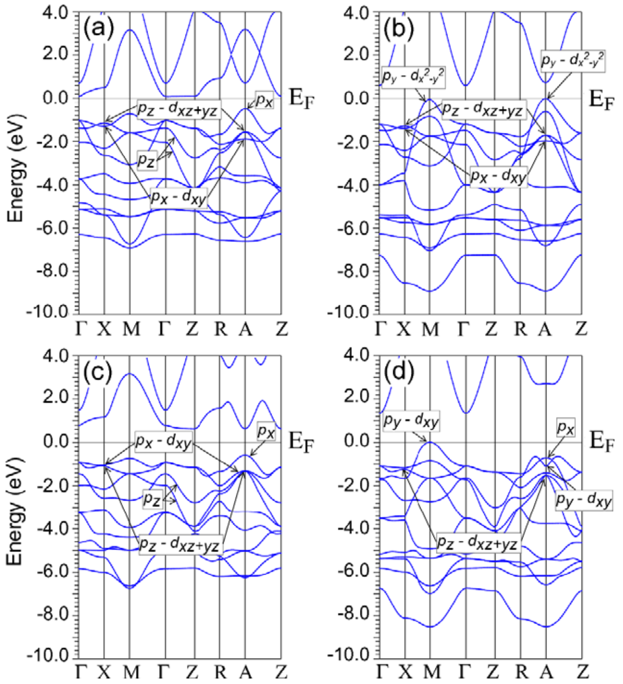

Figure 5. Electronic band structure of the simple tetragonal ((a), (b)) and high-pressure phases ((c), (d)) of $SrCuO_2$. Both spin-up ((a), (c)) and spin-down ((b), (d)) channels are shown. The orbital character of the bands is indicated in the figure.

From the analysis and comparison of the band structures described above, the out-of-plane instability of the O atoms shows a significant electronic origin. Similar results were obtained for $CaCuO_2$ by Savrasov *et al* [30] and Andersen *et al* [30, 31] using linear response calculations within DFT. They suggest that the out-of-plane distortion of the O atoms is necessary for the structural stability in the hole-doped $CaCuO_2$ as compared with the $SrCuO_2$ at high pressure.

4. Conclusions

In summary, the structure and energetics of the tetragonal $SrCuO_2$ phase and the recently determined tetragonal superstructure phase have been investigated based on *ab initio* calculations. The B3LYP hybrid density functional was used and this method correctly reproduced the unit cell parameters and the O-splitting in the superlattice structure. The energetic relation between the simple tetragonal structure and the tetragonal superstructure quantified the phase stability and kinetics of the phase transition. The result is consistent with experimental observations. The predictions based on the *ab* *initio* calculations, for instance the short-range ordering in the superstructure tetragonal phase, can be tested by experiment. The band structure calculations suggest that the out-of-plane buckling of the O atoms is important for the stability of the superstructure phase. The present theoretical results provide a fundamental understanding of the phase relations that are essential for synthesizing $SrCuO_2$.

Acknowledgments

JW and UB were supported by the National Science Foundation (NSF-NIRT, EAR-0403732), FZ and RCE by the Office of Basic Energy Sciences of the US Department of Energy (Grant DE-FG02-97ER45656). Computation was partially supported by the National Center for Supercomputing Applications under TG-DMR080047N and utilized the SGI Altix System.

References

[1] Zhang F X *et al* 2007 Pressure-induced splitting and buckling of Cu–O chains in the low-dimensional structure of $SrCuO_2$ *J. Am. Chem. Soc.* **129** 13923–6

[2] Feng X-B and Harrison N M 2004 Electronic structure of $CaCuO_2$ from the B3LYP hybrid density functional *Phys. Rev.* B **69** 132502

[3] Rice T M, Gopalan S and Sigrist M 1993 Superconductivity, spin gaps and luttinger liquids in a class of cuprates *Europhys. Lett.* **23** 445–9

[4] Norton D P *et al* 1994 Superconductivity in $SrCuO_2$-$BaCuO_2$ superlattices—formation of artificially layered superconducting materials *Science* **265** 2074–7

[5] Li Z Z *et al* 2009 Influence of oxygen reduction on the structural and electronic properties of electron-doped $Sr_{1-x}La_xCuO_2$ thin films *Physica* C **469** 73–81

[6] Bobrovskii V I *et al* 2004 Effect of high pressure on the crystal structure of $Sr_{1-x}La_xCuO_2$ compounds *Phys. Solid State* **46** 1438–41

[7] Feng S P *et al* 2008 Electronic structure of kinetic energy driven cuprate superconductors *Int. J. Mod. Phys.* B **22** 3757–811

[8] Azuma M *et al* 1992 Superconductivity at 110 K in the infinite-layer compound $(Sr_{1-x}Ca_x)_{1-y}CuO_2$ *Nature* **356** 775–6

[9] Kikkawa G E S *et al* 1992 Structural, electrical and magnetic studies of infinite-layered $Sr_{1-x}La_xCuO_2$ superconductor *Physica* C **196** 271–5

[10] Takano M *et al* 1989 Alkaline-earth CuO_2 crystallizing in a layered structure *Physica* C **159** 375–8

[11] Becke A D 1993 Density-functional thermochemistry. III. The role of exact exchange *J. Chem. Phys.* **98** 5648–52

[12] Saunders V R *et al* 2004 *Crystal 2003 User's Manual* (Torino: University of Torino)

[13] Singh D 1994 *Planewaves, Pseudopotentials, and the LAPW Method* (Boston: Kluwer Academic)

[14] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2K, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* ed T Universität Wien

[15] Habas M P, Dovesi R and Lichanot A 1998 The $B_1 \rightleftharpoons B_2$ phase transition in alkaline-earth oxides: a comparison of *ab initio* Hartree–Fock and density functional calculations *J. Phys.: Condens. Matter* **10** 6897–909

[16] Doll K and Harrison N M 2000 Chlorine adsorption on the Cu(111) surface *Chem. Phys. Lett.* **317** 282–9

[17] Towler M D *et al* 1994 *Ab initio* study of MnO and NiO *Phys. Rev.* B **50** 5041–54

[18] Podlesnyak A *et al* 1994 Synthesis, crystal-structure and inelastic neutron-scattering in the infinite-layer compounds $Sr_{1-x}Nd_xCuO_2$ *Physica* C **230** 311–7

[19] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple *Phys. Rev. Lett.* **77** 3865–8

[20] Anisimov V I *et al* 1993 Density-functional theory and NiO photoemission spectra *Phys. Rev.* B **48** 16929–34

[21] Ylvisaker E R, Pickett W E and Koepernik K 2009 Anisotropy and magnetism in the LSDA plus U method *Phys. Rev.* B **79** 035103

[22] Vaknin D *et al* 1989 Antiferromagnetism in $(Ca_{0.85}Sr_{0.15})CuO_2$, the parent of the cuprate family of superconducting compounds *Phys. Rev.* B **39** 9125

[23] Henkelman G, Uberuaga B P and Jonsson H 2000 A climbing image nudged elastic band method for finding saddle points and minimum energy paths *J. Chem. Phys.* **113** 9901–4

[24] Singh D, Pickett W E and Krakauer H 1989 Electronic structure of $CaCuO_2$, parent of the high-T_c superconductors *Physica* C **162–164** 1431–2

[25] Anisimov V I, Zaanen J and Andersen O K 1991 Band theory and mott insulators—Hubbard U instead of Stoner I *Phys. Rev.* B **44** 943–54

[26] Mei C and Smith V H Jr 1993 Electronic structure of $SrCuO_2$ doped with Ca *Physica* C **209** 389–92

[27] Agrawal B K and Agrawal S 1993 Structural, dynamical, and electronic properties of $CaCuO_2$ *Phys. Rev.* B **48** 6451

[28] Novikov D L, Gubanov V A and Freeman A J 1993 Electronic structure and Fermi surface topology of the infinite-layered superconductor $Sr_{1-x}Ca_xCuO_2$ *Physica* C **210** 301–7

[29] Weht R, Osvaldo Rodriguez C and Weissmann M 1994 *Ab initio* calculations of electronic band structure, nesting features of the Fermi surface and frozen phonons in the infinite layer cuprates *Physica* C **223** 339–46

[30] Savrasov S Y and Andersen O K 1996 Linear-response calculation of the electron-phonon coupling in doped $CaCuO_2$ *Phys. Rev. Lett.* **77** 4430

[31] Andersen O K *et al* 1996 Out-of-plane instability and electron–phonon contribution to s- and d-wave pairing in high-temperature superconductors; LDA linear-response calculation for doped $CaCuO_2$ and a generic tight-binding model *J. Low Temp. Phys.* **105** 285–304

[32] Wu H *et al* 1999 The electronic structure of $CaCuO_2$ and $SrCuO_2$ *J. Phys.: Condens. Matter* **11** 4637

[33] Lombardi A *et al* 1996 Temperature dependence of the sublattice magnetization of the antiferromagnet $Ca_{0.85}Sr_{0.15}CuO_2$ *Phys. Rev.* B **54** 93–6