Electronic structure of superoxygenated La$_2$NiO$_{4+\delta}$ domains with ordered oxygen interstitials

Thomas Jarlborg$^{1,2}$ and Antonio Bianconi$^{2,3,4}$

$^1$DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland
$^2$RICAMSS Rome International Center for Materials Science Superstripes, Via dei Sabei 119A, 00185 Rome, Italy
$^3$Institute of Crystallography, Consiglio Nazionale delle Ricerche, via Salaria, 00015 Monterotondo, Italy
$^4$INSTM, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, UdR Rome, Italy

The electronic structures of La$_2$NiO$_{4+\delta}$, where additional oxygen interstitials are forming stripes along (1,1,0), are presented. Spin-polarized calculations show that ferromagnetism on Ni sites is reduced near the stripes and enhanced far from the stripes. Totally the magnetic moment becomes reduced because of oxygen interstitials. It is suggested that the oxygen interstitial concentration in oxygen rich domains in nickelates suppress magnetism and give multiband metallic domains.

PACS numbers: 74.20.Fq, 74.72.-h, 74.25.Jb

I. INTRODUCTION.

Superoxygenated La$_2$NiO$_{4+\delta}$ is an oxygen ionic conductor at high temperature$^{[1,2]}$ with interesting electrochemical, thermo-mechanical properties and applications in fuel cells$^{[3,10]}$. The gas of mobile oxygen interstitials (O$_i$) at high temperature freeze below about 400K forming crystalline grains, as is observed by electron and neutron diffraction$^{[11,15]}$. At lower temperature, below 200K, the electronic structure show the onset of spin and charge stripes i.e., one dimensional spin density waves (SDW) and charge density waves (CDW)$^{[16,24]}$ due to ordering of polarons$^{[21]}$. Localized charges trapped by local lattice distortions (LLD) make periodic lattice distortions (PLD), as obtained by doping a magnetic Mott insulator La$_2$NiO$_4$. The polaronic CDW in La$_2$NiO$_{4+\delta}$ is therefore a model system to be compared with the more complex case in doped cuprates where polarons$^{[22,24]}$ coexist with free carriers$^{[25,27]}$ giving origin to Feshbach like resonances of polaron pairs and BCS pairs$^{[28–32]}$ in the superconducting phase. The other common feature of nickelates and cuprates is the electronic phase separation in multi-orbital strongly correlated systems which is predicted by the multiband Hubbard model in presence of long range Coulomb interaction$^{[33,34]}$. The stripe inhomogeneity of the lattice due to i) ordering of oxygen interstitials in ordered domains$^{[35]}$ ii) oxygen mobility at high temperature and the electron-lattice interaction at low temperature in nickelates and cuprates is controlled by the lattice constant of the CuO$_2$ or NiO$_2$ 2D atomic layers and the La$_2$O$_{2+\delta}$ blocks layers$^{[36,37]}$, which is key feature for the lattice stripes phase in cuprates$^{[38,39]}$.

La$_2$NiO$_{4+\delta}$ is isostructural with the widely studied La$_2$CuO$_{4+\delta}$ which could make its band structure very similar to optimally doped La$_2$CuO$_4$ (LCO)$^{[40,41]}$, even if the band filling is different. Ordering of excess oxygens in interstitial positions in LCO will also enhance $T_c$ $^{[35]}$, and the Fermi surface (FS) is shown to become fragmented by the oxygens$^{[42]}$. Moreover it is similar with other systems where oxygen interstitialities like in HgBa$_2$CuO$_{4+\delta}$ or oxygen vacancies like in Ba$_2$CuO$_{4−\delta}$ increases considerably $T_c$. $^{[43,45]}$ The electronic structure of oxygenated nickelates La$_2$NiO$_{4+\delta}$ is not known. For instance it is not established that ferromagnetism (FM) can be suppressed and allow for superconductivity in these materials. The equivalence of spin-phonon coupling in the cuprates, where phonons can enforce spin waves$^{[46]}$, is not known. It can lead to fluctuations of local moment amplitudes as in other FM materials.$^{[47,48]}$ Therefore it is of high interest to calculate the electronic structure of the domains present in La$_2$NiO$_{4+\delta}$ below 400K with a stoichiometric content of oxygen interstitials. In this work we present electronic structure results for the highly hole doped puddles of oxygen interstitials in superoxygenated La$_2$NiO$_4$, ordered into stripes along (1,1,0) mostly separated by 3 unitcells. The method of calculation is presented in sect. II. Experimental information on oxygen ordering is used to define the supercells of O-rich LNO, as discussed in sect. II. In sect. III we discuss the results of the calculations, and some ideas for future works are given together with the conclusions in sect. IV.

II. METHOD OF CALCULATION.

The calculations are made using the linear muffin-tin orbital (LMTO)$^{[49,50]}$ and the local spin-density approximation (LSDA)$^{[51]}$. The details of the methods have been published earlier$^{[42,52,56]}$. The elementary cell of La$_2$NiO$_4$ (LNO) contains La sites at (0,0,±21c), Ni at (0,0,0), planar O’s at (0.5,0,0) and (0.5,0) and apical O’s at (0,0,±366c), in units of the lattice constant $a_0=3.86\ A$, where $c=1$. In addition to the MT-spheres at the atomic sites we insert MT-spheres at positions (5,0,±5c) and (0,5,±5c) to account for the positions of empty spheres.

The atomic sphere radii are 1.75 A (La), 1.25 A (Cu), 1.17 A (planar oxygens, oxygen, interstitials, O$_i$, and empty spheres), and 1.20 A (apical oxygens), respectively. Six units of the elementary cell La$_2$NiO$_4$ are...
TABLE I: Decomposition of the total DOS at $E_F$ on each of the six Ni atoms in La$_{12}$Ni$_6$O$_{24}$ (LNO-1) and La$_{12}$Ni$_6$O$_{24}$ (LNO-0) (in units of (cell · eV)$^{-1}$), magnetic moment per site, $m$, ($\mu_B$ per site), and number of valence electrons per Ni site, $Q$. The total magnetic moment in the LNO-0 cell is 1.32 $\mu_B$ and in LNO-1 0.76 $\mu_B$. The interstitial site in LNO-1 is at the $y$-layer between site 1 and 2.

| Site | $m$ ( $\mu_B$ ) | $Q$ (eV) |
|------|----------------|----------|
| 1    | 1.2            | 0.09     |
| 2    | 1.0            | 0.10     |
| 3    | 2.4            | 0.11     |
| 4    | 2.6            | 0.12     |
| 5    | 2.4            | 0.11     |
| 6    | 1.6            | 0.10     |

TABLE II: The local decomposition of the DOS at $E_F$ on the different Ni sites in La$_{33}$Ni$_6$O$_{24}$ (LNO8-1) and La$_{33}$Ni$_6$O$_{24}$ (LNO8-2). The last column shows the total DOS per cell, all in units of (cell · eV)$^{-1}$). Site 1 is nearest to the oxygen interstitials, site 5 is most distant, and the other sites are counted pairwise as function of increasing distance from the O-rich layer.

| Site | $N$($E_F$) | $m$ | $Q$ |
|------|------------|-----|-----|
| 1    | 1.3        | 0.03| 0.20|
| 2    | 0.8        | 0.25| 0.19|
| 3    | 1.9        | -0.02| 0.18|
| 4    | 2.4        | 0.10| 0.18|
| 5    | 2.7        | 0.15| 0.15|

FIG. 1: (Color online) The total DOS for La$_{16}$Ni$_8$O$_{32+N}$ with $N$=0 and $N$=1.

FIG. 2: (Color online) The total DOS for La$_{16}$Ni$_8$O$_{32+2}$ with $N$=0, 1 and 2.

The empty sites at the interstitial positions are occupied by the excess oxygen ion. These supercells are chosen in order to represent fairly well the experimentally determined structures [57]. The basis set goes up through $\ell=2$ for all sites. The $z$-projected IBZ (irreducible Brillouin zone) corresponding to the supercell is shown in Fig. 3 by the limits $\Gamma$ to $\Delta$ or $X_3$ or $R$. It corresponds to one third (folded) BZ for antiferromagnetic (AFM) LCO. Paramagnetic and spin-polarized calculations are made for these cells. Self-consistency is made with 192 k-points and final results are based on 702 points in the IBZ.

No interstitial sites are occupied with O in one set of the calculations (called LNO-0). The LNO-0 results serve as a reference for comparison with the results with oxygen interstitials. For instance, the FS for (undoped) LNO forms a circle centered at the $\Gamma$ point in BZ of the elementary cell, but since the BZ corresponding to the supercell is folded and very flat along the Ni-O bond direction (1,0,0). The band calculations are made for this supercell containing 54 sites totally, where one of the empty sites at the interstitial positions is occupied by the excess oxygen ion. These supercells are chosen in order to represent fairly well the experimentally determined structures [57]. The basis set goes up through $\ell=2$ for all sites. The z-projected IBZ (irreducible Brillouin zone) corresponding to the supercell is shown in Fig. 3 by the limits $\Gamma$ to $\Delta$ or $X_3$ or $R$. It corresponds to one third (folded) BZ for antiferromagnetic (AFM) LCO. Paramagnetic and spin-polarized calculations are made for these cells. Self-consistency is made with 192 k-points and final results are based on 702 points in the IBZ.

No interstitial sites are occupied with O in one set of the calculations (called LNO-0). The LNO-0 results serve as a reference for comparison with the results with oxygen interstitials. For instance, the FS for (undoped) LNO forms a circle centered at the $\Gamma$ point in BZ of the elementary cell, but since the BZ corresponding to the supercell is folded and very flat along the Ni-O bond direction (1,0,0) it is necessary to identify the circle from several FS pieces in the folded zone. In the second set of calculations we insert one oxygen (La$_{12}$Ni$_6$O$_{24+1}$, LNO-1) at an interstitial position to calculate the electronic structure of a La$_2$NiO$_{4.166}$ domain.

Paramagnetic calculations were also made for La$_{16}$Ni$_8$O$_{32+2}$ by putting together 8 elementary cells of La$_2$NiO$_4$ to calculate the electronic structure of a La$_2$NiO$_{4.125}$ domain. Totally there are 72 sites in these supercells, and $N =$0, 1 or 2 interstitial oxygens are inserted (LNO8-0, LNO8-1 and LNO8-2, respectively). These cells are of equivalent size as the cells that was used for the studies of electronic structures of interstitial O in LCO [42], which is helpful for direct comparisons between the nickelates and cuprates. An important
difference between LNO and LCO is that there is one less filled d-band per metal atom. In the largest cell of LNO8-0 there are 208 occupied bands, in LCO8-0 there are 212. Here, for LNO we concentrate the investigations of the shorter cells, since they correspond best to the experimentally found periodicity of O-interstitials in LNO [11,12].

The excess $O_i$’s sit at the interstitial interlayer positions, above the oxygen ion in the NiO$_2$ plane of the orthorhombic unit cell. The insertion of $O_i$’s is expected to induce hole doping, because each new oxygen interstitial will bring 4 new bands well below $E_F$ (one "s" and 3 "p"), but the oxygen has only 2 "s" and 4 "p" electrons. Therefore, simple arguments suggest that one Ni-O band becomes unfilled, i.e. $E_F$ has to go down relative to the rest of the bands. However, other atoms like La serve as charge reservoirs, lattice reconstructions are likely, and in addition the excess O positions are ordered in stripe-like patterns like in La$_2$CuO$_{4+\delta}$ [57].

Correlation is not expected to be an issue for cuprates and nickelates with hole doping larger than 0.2 holes per Cu (or Ni) site away from half-filling of the d-band. This makes the DOS large in undoped NiO$_2$ [62], and it goes down rapidly for the next layers, and reaches $\sim 0.5$ per cell for the most distant Ni site. The differences in local $N(E_F)$ are also reflected in the local moments on Ni, as can be expected from the DOS at $E_F$ and the criterion for Stoner magnetism. Ferromagnetism (FM) tends to disappear near layers with interstitial O. The moment on the Ni site close to the $O_i$-site is practically zero, and in the next Ni layers the moments are even slightly negative. Further away the moments become clearly FM again, and their amplitude are even larger (0.2-0.25 $\mu_B$) than the moment per Ni-site in undoped LNO (0.18 $\mu_B$). The obvious question is whether FM in nickelates is responsible for the absence of superconductivity in LNO. However, the domains with increased $O_i$-concentrations made of ordered $O_i$-stripes show weaker FM, but they are still metallic with a different multiband FS from what is found in LCO superconductors.

The main difference between LCO and LNO with oxygen interstitials, is due to the fact that Ni has one electron less than Cu. Thus, LNO is like a heavily hole doped version of LCO with $E_F$ pushed down within the high DOS of the 3d-bands. This makes the DOS large in undoped LNO, sufficiently large for Stoner magnetism, while this is not the case in LCO [53]. The changes of the effective charges (see Table 1) show a weak hole doping on Ni when the number of $O_i$ increases. The same trend is found in the LNO8 results, and it is in agreement with the behavior for LCO.

In Figs. 3 are displayed the FS pieces in different $k_z$-planes of the irreducible BZ for LNO-0 and LNO-1, respectively. For the calculations without oxygen interstitial it is easy to recognize simple $\Gamma$-centered FS circles in the unfolded BZ, as for LCO [12]. There are minor

![FIG. 3: (Color online) Upper panel: The Fermi surface of band 157 (upper panel) and band 156 (lower panel) for non-magnetic La$_{12}$Ni$_6$O$_{24}$ indicated by k-points ($k_x,k_y,k_z$) for which $E(k)$ is within 0.01 eV from $E_F$. The different marks indicate three different levels of $k_z$. The limits of the rectangular IBZ of the supercell given by the rectangle $\Gamma$-M$_1$-X$_1$-R.

Unfolding the FS of band 156 leads to circular FS within the IBZ elementary cell.](image-url)
modifications in different $k_z$ planes because of a weak 3-D dispersion. The diameter of the circles is smaller than in undoped LCO. As for stripes in LCO, the FS’s become segmented and show gaps when there are $O_i$ stripes, and it becomes more difficult to visualize their projection in an unfolded zone.

IV. CONCLUSION.

Oxygen interstitials forming of atomic stripes in the spacer layers form three overlapping mini-bands crossing $E_F$ making the local Ni-d DOS larger on sites far from the $O_i$-stripes. Near the stripes the local Ni-d DOS is reduced. The consequence is that FM is enhanced between the stripes and almost quenched at the stripes. Thus, the natural growth of $O_i$-stripes in the oxygen rich domains seems to be an efficient way to suppress FM in the nickelate, and if the method can be optimized it might be a path for making the nickelates good metals. It can be noted that suppression of FM is one of the requirements for superconductivity. The band structures in LNO and LCO are different because of the different band filling, but the evolution of the FS’s in undoped and oxygenated LNO behave quite similarly as in LCO. The undoped material has simple FS’s much like the ones for supercells of stoichiometric LCO despite the large differences of d-band filling between Cu and Ni. Finally we have shown that oxygen interstitials order breaks up the FS’s into fragments with gaps in between, similar to the process in oxygenated LCO [42].

[1] S. Y. Jeon, M. B. Choi, H. N. Im, J. H. Hwang, and S. J. Song, Journal of Physics and Chemistry of Solids 73, 656 (2012).
[2] Z. Li, R. Haugsrud, and T. Norby, Solid State Ionics 184, 42 (2011).
[3] A. Chroneos, R. V. Vovk, I. L. Goulatis, and L. I. Goulatis, Journal of Alloys and Compounds 494, 190 (2010).
[4] M. Burriel, G. Garcia, J. Santiso, J. A. Kilner, R. J. Chater, and S. J. Skinner, J. Mater. Chem. 18, 416 (2008).
[5] V. V. Kharton, A. P. Viskup, E. N. Naumovich and F. M. B. Marques, J. Mater. Chem. 9, 2623 (1999).
[6] A. Chroneos, D. Parfitt, J. A. Kilner, and R. W. Grimes, J. Mater. Chem. 20, 266 (2010).
[7] L. Lu, Y. Guo, H. Zhang, and J. Jin, temperature solid oxide fuel cells Materials Research Bulletin 45, 1135 (2010).
[8] B. X. Huang, J. Malzbender, R. W. Steinbrech Journal of Materials Science 46, 4937–4941 (2011).
[9] S. Y. Jeon, M. B. Choi, J. H. Hwang, E. D. Wachsman, and S.-J. Song, Journal of Solid State Electrochemistry 16, 785 (2012).
[10] A. M. Henderson, L. Mogni, and A. Caneiro, International Journal of Hydrogen Energy 35, 6031 (2010).
[11] Z. Hiroi, T. Obata, M. Takano, Y. Bando, Y. Takeda, and O. Yamamoto, Physical Review B 41, 11665 (1990).
[12] M. Sayagues, M. Vallet-Regi, J. L. Hutchison, and J. M. Gonzalez-Calbet, Journal of Solid State Chemistry 125, 133 (1996).
[13] W. Paulus, A. Cousson, G. Dhalenne, J. Berthon, A. Revcolevschi, S. Hosoya, W. Treutmann, G. Heger, and R. Le Toquin, Solid State Sciences 4, 565 (2002).
[14] M. Huecker, K. Chung, M. Chand, T. Vogt, J. M. Tranquada, and D. J. Buttrey, Physical Review B 70, 064105 (2003).
[15] T. Klande, K. Efimov, S. Cusenza, K.-D. Becker, and A. Feldhoff, Journal of Solid State Chemistry 184, 3310 (2011).
[16] I. M. Abu-Shiekah, O. Bakharev, H. B. Brom, and J. Zaanen, Physical Review Letters 87, 237201 (2001).
[17] C. C. Homes and J. M. Tranquada, Physical Review B 52, 3581 (1995).
[18] J. M. Tranquada, J. E. Lorenzo, D. J. Buttrey, and V. Sachan, Physical Review B 75 045128 (2007).
[19] J. M. Tranquada, J. E. Lorenzo, D. J. Buttrey, and V. Sachan, Physical Review B 52, 3581 (1995).
[20] N. Poirot, R. A. Souza, and C. M. Smith, Solid State Sciences 7, 1157 (2005).
[21] J. Zaanen, P. Littlewood Physical Review B 50, 7222 (1994). doi:10.1103/physrevb.50.7222
[22] A. Bianconi, M. Missori, H. Oyanagi, H. Yamaguchi, Y. Nishiara, and S. Della Longa, EPL (Europhysics Letters) 31, 411 (1995).
[23] A. Bianconi and M. Missori, Solid State Communications 91, 287 (1994).
[24] A. Bianconi, Physica C 235-240, 269 (1994).
[25] A. Bianconi, D. Di Castro, G. Bianconi, A. Pifferi, N. L. Saini, F. C. Chou, D. C. Johnston, and M. Colapietro, Physica C: Superconductivity 341, 1719 (2000).
[26] A. Bianconi, International Journal of Modern Physics B 14, 3289 (2000).
[27] N. Poccia, A. Ricci, G. Campi, M. Fratini, A. Puri, D. Di Gioacchino, A. Marcelli, M. Reynolds, M. Burghammer, N. L. Saini, et al., Proceedings of the National Academy of Sciences 109, 15685 (2012).
[28] A. Bianconi, A. Valletta, A. Perali, and N. L. Saini, Solid State Communications 102, 369 (1997).
[29] A. Bianconi, Journal of Superconductivity 18, 625 (2005).
[30] M. Fratini, N. Poccia, and A. Bianconi, Journal of Physics: Conference Series 108, 012036 (2008).
[31] A. Bianconi, Nature Physics 9, 536 (2013).
[32] K. I. Kugel, A. L. Rakhmanov, A. O. Sboychakov, N. Poccia, and A. Bianconi, Phys. Rev. B. 78, 165124 (2008).
[33] A. Bianconi, N. Poccia, A. O. Sboychakov, A. L. Rakhmanov, and K. I. Kugel, Superconductor Science and Technology 28, 024005 (2015).
[34] N. Poccia, M. Fratini, A. Ricci, G. Campi, L. Barba, A. Vittorini-Orgeas, G. Bianconi, G. Aeppli, and A. Bianconi, Nature Materials 10, 733 (2011).
[35] D. Di Castro, G. Bianconi, M. Colapietro, A. Pifferi, N. L. Saini, S. Agrestini, and A. Bianconi, The European Physical Journal B - Condensed Matter and Complex Systems 18, 617 (2000).
[36] A. Bianconi, S. Agrestini, G. Bianconi, D. Di Castro, and N. L. Saini, Journal of Alloys and Compounds 317-318, 537 (2001).
[37] J. C. Phillips, Journal of Superconductivity and Novel Magnetism 27, 345 (2014).
[38] G. Campi et al. Nature (2015) in press
[39] T. Jarlborg, B. Barbiellini, R.S. Markiewicz and A. Bansil, Phys. Rev. B 86, 235111 (2012).
[40] T. Jarlborg, A. Bianconi, B. Barbiellini, R.S. Markiewicz, A. Bansil, J. Supercond. Nov. Magn. 26, 2597 (2013).
[41] T. Jarlborg and A. Bianconi, Phys. Rev. B 87, 054514, (2013).
[42] W.B. Gao, Q.Q. Liu, L.X. Yang, Y. Yu, F.Y. Li, C.Q. Jin and S. Uchida, Phys. Rev. B 80, 094523 (2009)
[43] T.H. Geballe and M. Marezio, Physica C 469, 680, (2009).
[44] O. Chmaissem, I. Grigoraviciute, H. Yamauchi, M. Karpinnen and M. Marezio, Phys. Rev. B 82, 104570, (2010).
[45] T. Jarlborg, Physica C454, 5, (2007).
[46] T. Jarlborg, Phys. Rev. B 89, 184426 (2014).
[47] T. Jarlborg, Phys. Rev. B 59, 15002, (1999).
[48] O.K. Andersen, Phys. Rev. B12, 3060 (1975).
[49] B. Barbiellini, S.B. Dugdale and T. Jarlborg, Comput. Mater. Sci. 28, 287 (2003).
[50] O. Gunnarsson and B.I. Lundquist, Phys. Rev. B 13, 4274 (1976).
[51] T. Jarlborg, Phys. Rev. B64, 060507(R), (2001).
[52] B. Barbiellini and T. Jarlborg, Phys. Rev. Lett. 101, 157002, (2008).
[53] T. Jarlborg, Phys. Rev. B76, 140504(R), (2007).
[54] T. Jarlborg, Appl. Phys. Lett. 94, 212503, (2009).
[55] T. Jarlborg, Phys. Rev. B84, 064506, (2011).
[56] M. Fratini, N. Poccia, A. Ricci, G. Campi, M. Burghammer, G. Aeppli, and A. Bianconi, Nature 466, 841 (2010).
[57] B. Barbiellini, P. Genoud, Y. Henry, L. Hoffmann, T. Jarlborg, A.A. Manuel, S. Massidda, M. Peter, W. Sadowski, H.J. Scheel, A. Shukla, A.K. Singh and E. Walker, Phys. Rev. B 43, 7810 (1991).
[58] W.E. Pickett, Rev. Mod. Phys. 61, 433 (1989).
[59] A. Damascelli, Z.-X. Shen and Z. Hussain, Rev. Mod. Phys. 75, 473, (2003).