Mimicking superconducting cuprates with square-planar layered nickelates

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ABSTRACT

In the wake of the discovery of the *very first* nickel superconductor in 2019, the question of alternative high-T_c superconductors to that of the cuprates – who dominate that class – is at the forefront of condensed matter physics. Presented here is a preliminary step in further studying a family of rare-earth nickelate candidates and their electronic structure, a benchmark set by limited experimental data. The atomic and electronic structure for Ruddlesden-Popper parents $\mathbf{RO(RNiO_3)_n}$ from first-principles calculations provide an introductory analysis to ideal candidates for cuprate-like superconductors.

Introduction

The primary mechanism behind high-temperature superconductivity is a tremendous challenge in the field of condensed matter physics. The range of materials that exhibit this extraordinary phenomenon is largely dominated by layered cuprate compounds. A strategy to finding novel high-T_c superconductors is to design systems with similar electronic structure. Layered nickelates are good candidates because they too are quasi-two dimensional square planar lattices, and they have the potential to demonstrate some hallmark characteristics of the cuprates: strong antiferromagnetic correlations, large orbital polarization of the unoccupied e_g states (with d orbitals near the Fermi energy), strong $p-d$ hybridization, and multiple broken symmetry phases.

The family of rare-earth compounds, $R_{n-1}(NiO_2)_nR_2O_2$, where R = La, Pr have been studied for $n \leq 3$. For $n = 3$, R = La is insulating due likely to strip formation (an unbroken symmetry phase). R = Pr is metallic down to 2K due to what is thought to be a "chemical pressure effect," that is, Pr^{3+} is smaller than La^{3+} [1]. There is motivation to study the higher orders, $n > 3$, because the number of $3d$ electrons correspond to superconductivity in analogous cuprate structures (see *Figure 1)*.

An additional obstacle for studying these layered candidates is their inability to be grown in the lab. What *can* be grown are Ruddlesden-Popper (RP) parent phases, those which retain apical oxygens (oxygens on top of Ni). These phases reduce to the square planar phase via oxygen reduction. Like the square planar cases, $n > 3$ have not been studied.

The RP parent phase, $RO(RNiO_3)_n$, for the case $n = 4$ has recently been grown from molecular beam epitaxy, so the $n = 4$ square planar compound is experimentally feasible [6]. While there are no experiments to date, this hypothetically extends to $n = 5, 6$, providing a sound basis for theoretical inquiry: a study of the trends of electronic structure in the RP phases of these compounds.

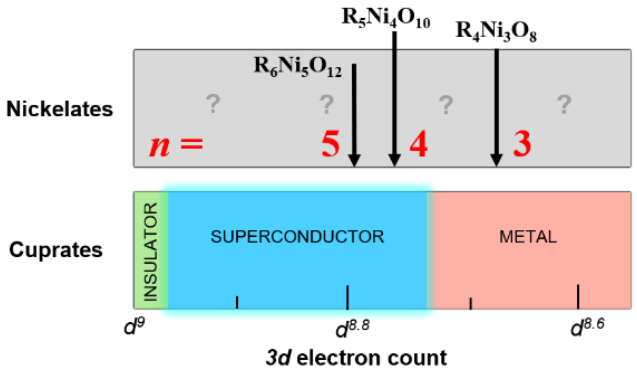

Figure 1: *Plotting the 3d electron count widely-studied cuprates against the nickelates, it is apparent that a similar electronic structure will yield superconductivity for $n = 4, 5$.*

Methodology

A study of materials reduces to a many-body quantum mechanics problem. But the Schrödinger equation (SE) quickly becomes intractable for elements with more than a few electrons. The electronic structure was examined using density functional theory (DFT). DFT relies on the Hohenberg-Kohn theorem, which dictates the electronic density yields the same observable quantities as the SE. Though the formalism behind DFT is exact, the main approximation is of the exchange-correlation interaction between electrons. The Perdew–Burke–Ernzerhof exchange-correlation functional was used on a $16 \times 16 \times 4$ electronic momentum $\mathbf{k}$-mesh, with 0.005 eV Gaussian smearing. Volumetric relaxations were performed using the Vienna ab-initio simulation package (VASP).

Electronic bandstructure and density of states calculations were performed with the full-electron, LAPW code WIEN2k.

Results and discussion

For the case of $n = 3$, R = La, experimental RP structure with the *Bmab* (No. 64) symmetry was obtained from [1]. Our task was to determine a benchmark for the higher orders from the $n = 3$ compound. For this case, a tetragonal cell with *I4/mmm* (No. 139) symmetry was constructed, and relaxation of the lattice parameters and internal coordinates was performed while including various degrees of broken symmetry. While the distortions of the oxygen tetrahedra was achieved in agreement with the experimental structure with the *Bmab* (No. 64) symmetry, the symmetry of the structure was lowered further to *P2* (No. 2). With symmetrical oxygen sites preserved, the structure with the *I4/mmm* symmetry was relaxed to similar internal bond lengths and out-of-plane length c to that of the experimental structure with the *Bmab* symmetry, but the symmetry still reduced to *Pmmm* (No. 47). Bands and density of states (DOS) calculations were performed on this structure with the *Pmmm* symmetry to examine the benchmark for higher order, $n > 3$ calculations, for which no experimental data is yet available.

Our current benchmark provides valuable insight as to how examine electronic structure for the higher orders. In general, the bandstructures of the modelled and experimental structures look similar but are distinct in band number and crossings (see *Figure 2*). These are both things that can be improved upon, however, in future work.

We also study the DOS for Ni orbital characters for both the modelled and experimental structure (see *Figure 3*). The $d_{x^2-y^2}$ and d_{z^2} orbitals are close to the Fermi energy – a feature commonly observed in cuprates – motivating a study of these trends for higher orders.

Conclusion and future work

The goal of this summer work was to establish a suitable benchmark for inquiry of higher order RP and square planar nickelate compounds, the latter of which are strong candidates for high- T_c superconductivity. Having scrutinized the benchmark-compound in question, $n = 3$, a continued analysis of $n = 4, 5$, and 6 will be performed once symmetry concerns and precision requirements are addressed. This means improving structural input for WIEN2k and VASP, as well as performing more demanding calculations (increasing the number of **k**-points). Precision near the Fermi level for electronic bandstructure and DOS will likely be improved with these more costly calculations, with finer **k**-mesh convergence.

Furthermore, a systematic approach will be useful because the mechanism(s) responsible for high-T_c superconductivity is still a mystery. Examining this trend of orbital characters in comparison to the experimental benchmark is of interest, in addition to the bandstructure of these higher order nickelates.

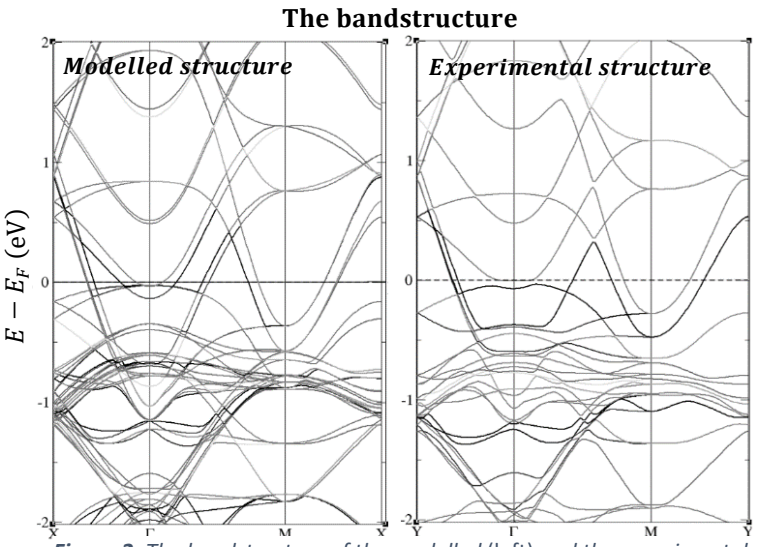

Figure 2: *The bandstructure of the modelled* (left) *and the experimental structure* (right)*. Generally, the bandstructure is a decent match, but the bands are split, and the crossings are disparate for the modelled structure.*

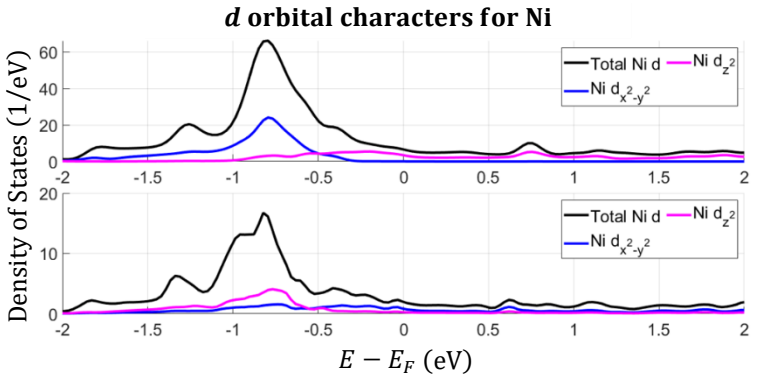

Figure 3: *The density of states for the modelled (top) and the experimental structure (bottom). Both* Ni d *orbitals dominate the Fermi surface.*

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References:

1. J Zhang, A. S. Botana, J. W. Freeland, D. Phelan, H. Zheng, V. Pardo, M.R. Norman and J.F. Mitchell. *Nature Physics* **13**, 864 (2017).
2. H. Li, X. Zhou, T. Nummy, J. Zhang, V. Pardo, W. E. Pickett, J. F. Mitchell, and D. S. Dessau. *Nature Communications* **8**, 704 (2017).
3. A. S. Botana, V. Pardo, and M. R. Norman. *Phys. Rev. Materials* **1**, 021801(R) (2017).
4. Schwarz, K. & Blaha, P. *Comput. Mater Sci.* **28**, 259–273 (2003).
5. Perdew, J. P., Burke, K. & Ernzerhof, M. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
6. Lei, Q., Golalikhani, M., Davidson, B.A. et al. *npj Quant Mater 2*, **10** (2017).