Transport properties of the parent LaNiO$_2$

Mijanur Islam$^{1,a}$, Sudipta Koley$^2$, and Saurabh Basu$^1$

1 Department of Physics, Indian Institute of Technology-Guwahati, Guwahati 781039, India
2 Department of Physics, Amity Institute of Applied Sciences, Amity University Kolkata, Kolkata 700135, India

Received 11 June 2021 / Accepted 13 September 2021 / Published online 22 September 2021
© The Author(s), under exclusive licence to EDP Sciences, SIF and Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract. Here, we study the transport properties of a nickelate compound, namely LaNiO$_2$ using density functional theory (DFT) in conjunction with dynamical mean field theory (DMFT). An interacting multi-orbital spin-resolved scenario for LaNiO$_2$ yields a metallic ground state with ferromagnetic correlations. The latter contrasts an antiferromagnetic order reported earlier. The metallic behaviour persists even at large values of the interaction energies. Further support of the metallic state is provided by the angular resolved photoemission spectroscopy (ARPES) data.

1 Introduction

Transport properties of strongly correlated compounds may yield many surprising features, such as non-Fermi liquid behaviour, strong magnetic correlations, the emergence of superconductivity, etc. The nickelates, namely, RNiO$_2$ (R = La, Nd) owing to their prospects of being compared (and contrasted) with the cuprates have started receiving significant attention in recent times. The realization of a superconducting phase in Sr-doped NdNiO$_2$ with a transition temperature in the range 9–15 K [1] rendered support to closer scrutiny on the similarity with the cuprates.

The rationale behind drawing a parallel between the nickelates and the cuprates is in the fact that Ni shares a close proximity of Cu in the periodic table. In fact, the infinite layer RNiO$_2$ is isostructural to CaCuO$_2$ [2–4], where the latter represents the parent compound of a high -T$_c$ superconductor. However, the parent compounds of nickelates are reported to be metallic with no magnetic order [1,4–7]. The absence of magnetic order is attributed to the 3d bands of Ni getting self-populated by holes from the 5d electrons of R resulting in no magnetic order. Indeed, in this sense, the nickelates are quite different than the cuprates. However, the hybridization between the d$_{x^2−y^2}$ orbitals of Ni and those of the rare earths (R) could be quite weak and the self-doping effects may not be dominant.

Valence counting of Ni$^{1+}$ cations with a 3d$^0$ configuration is formally similar to Cu$^{2+}$ in the cuprates [8]. The band structure predominantly consists of 3d$_{x^2−y^2}$ orbitals of Ni (similar to Cu d-orbitals) and 5d$_{x^2−y^2}$ orbitals from La with the contribution coming from the oxygen p-orbitals to be significantly less than that in the cuprates [6,9,10]. In the scenario presented by this, the hopping within the d-orbitals of Ni is negligible, and so are the inter-cell hopping amplitudes severely suppressed. In view of this, we have only retained the inter-orbital Coulomb repulsion between the 3d bands of Ni with those of 5d of La.

Before one understands the effects of doping, a few things need to be settled for the parent compound itself. With a view to accomplish that, we investigate the band structure and the transport properties of LaNiO$_2$ via DFT plus DMFT technique. While we agree on a metallic ground state and absence of any insulating behaviour (unlike cuprates) even at significantly large electronic correlations, our results on the magnetic behaviour disagrees with those in Ref. [11]. We distinctly get ferromagnetic correlations due to the Ni atoms via magnetization studies where the magnetic moments of the order of $\sim 0.28 \mu_B$ in the limit of vanishing field. This result severely contradicts the corresponding scenario in cuprates which has an antiferromagnetic insulating ground state for the undoped compound. This certainly holds a promise that the dopant-induced superconducting state may yield new physics embedded therein. Furthermore, a test of the familiar Fermi liquid (FL) theory in the context of the metallic ground state is probed by the peak in the single-particle Green’s function that can be verified by angular resolved photoemission spectroscopy (ARPES) experiments.

Our paper is organized as follows. We present the DFT band structure along with the crystal structure of nickelate LaNiO$_2$. The density of states (DOS) at the Fermi level is presented to confirm the existence of the metallic behaviour which are further supported by a T$^2$ resistivity that are demonstrated by the experiments [5,12]. As a test of the ferromagnetic correlations, we present the magnetization data as a function of the applied magnetic field and finally, the presence of the...
quasiparticle peaks provide support to the presence of the FL state.

2 Computational details

In this work, we have carried out density functional theory (DFT) calculations within Perdew–Burke–Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) [13] as implemented in Vienna ab initio Simulation Package (VASP) [14] to obtain the band structure and the density of states (DOS) of LaNiO$_2$. Furthermore, we use first-principles DFT combined with dynamical mean field theory to obtain the correlation effects of LaNiO$_2$ and should work for nickelates as well and with the values of the interaction parameters used in the recent studies [15,16], the results corresponding to nickelates were successfully reproduced the leading order terms of the self energy in all of the different cases, such as, in the weak coupling limit, the atomic limit, large frequency limit and it must be exact in the low frequency limit. In the IPT approximation, we approximate the self energy by its second-order contribution, namely,

$$\Sigma(\omega) \approx U n + \tilde{\Sigma}^{(2)}_0(\omega)$$

(3)

here $\tilde{\Sigma}^{(2)}_0(\omega)$ is the second order contribution arising due to the perturbation term, $H_{\text{int}}$ (see Eq. 1) and $n$ is the particle number. Though it is an approximate method, it gives good qualitative agreement compared to more exact methods to solve an interacting Hamiltonian.

Furthermore, in our DMFT with IPT approach, we determine the double counting by assuming the exact chemical potential for the system. Here, we used Luttinger theorem [33], or equivalently, the Friedel sum rule [34] in IPT to fix the particle number. In Luttinger theorem, there is a functional $\Phi[G]$ which can be represented by a set of diagrams containing only $G$ lines. The functional derivative of $\Phi$ with respect to $G$ yields the self-energy. The functional is invariant under a frequency shift in $G(i\omega)$; that is,

$$G(i\omega) \rightarrow G'(i\omega) = G(i\omega + i\lambda) = G(i\omega) + i\lambda \frac{\partial G(i\omega)}{i\omega} + O(\lambda^2).$$

(4)

From there, one can get the Luttinger theorem, namely,

$$\int_{-i\infty}^{i\infty} \frac{d\omega}{2\pi i} \frac{\partial \Sigma(\omega)}{\partial \omega} G(\omega) = 0.$$
Crystal structure of LaNiO$_2$. Green, black and red spheres represent La, Ni and O atoms respectively.

The calculated band structure is shown by DFT within the GGA approximation. The blue and the red lines represent the $\uparrow$- and the $\downarrow$-spin bands respectively.

The parameters, namely, the Coulomb interaction, $U_1$ and the Hund’s coupling, $J_H$ are varied within an experimentally realizable range to obtain the DOS in presence of electron correlation. Also, $\beta (=1/k_B T)$ is the inverse temperature. $T$ is varied up to 300 K to get the temperature dependent behaviour of the resistivity. The DFT plus DMFT self energy calculations are converged up to a precision of $10^{-4}$ in energy units.

3 Results and discussion

In Fig. 1a, we present the crystal structure of LaNiO$_2$. The crystal structure of LaNiO$_2$ is identical with NdNiO$_2$ (La replacing Nd). Figure 1b represents the spin-polarized DFT band structure of the given material. The blue and the red lines denote the $\uparrow$- and the $\downarrow$-spin bands, respectively. We see from our DFT calculation that near the Fermi energy only Ni 3d ($3d_{x^2-y^2}$) and La 5d ($5d_{3z^2-r^2}$) bands are present. The 2p bands of oxygen are well separated from them, which is in high contrast with its cuprate counterpart CaCuO$_2$ [11]. Now, from the non-interacting density of states obtained from the DFT calculations, we concentrate only on the four bands among all the atomic bands of LaNiO$_2$ that cross the Fermi level. These four bands are La (5d $\uparrow$), La (5d $\downarrow$), Ni (3d $\uparrow$), and Ni (3d $\downarrow$) bands.

The DOS is given by

$$D(\omega) = -\frac{1}{\pi} \text{Im} G(\omega).$$

In Fig. 2, we show the orbital-resolved spin-polarized density of states for the La 5d (Fig. 2a) and Ni 3d (Fig. 2b) atoms computed for various intra- and inter-band interaction energies $U_1$ and $U_2$. The results of the LDA+$U$ calculations on nickelates reported by Anisimov et al. [8] indicated it to be a stable antiferromagnetic insulator. However, the insulating nature of the ground state was contrasted by other groups [9,11] we too get a metallic behaviour. Though strong electronic correlations renormalize the DOS, the effects are not well visible at the scale presented here. From Fig. 2, it is observed that the spectral weight at the Fermi level, $E_F$, reduces with increasing $U$’s for all the four bands under consideration.

The correlated electronic spectra from the DMFT demonstrates that LaNiO$_2$ is a strongly correlated metal. The metallic behaviour for both the La and the Ni atoms with $\uparrow$- and $\downarrow$-spins were confirmed by vanishing of the imaginary part of the self-energy (Im$\Sigma(\omega)$) in the vicinity of the Fermi level ($E_F$). The imaginary part being zero implies the absence of a gap opening at the Fermi level, which, in our case remains robust up to moderate to high values of the interaction potential ($U_1$ and $U_2$). To avoid repetition, we only plot...
ImΣ(ω) corresponding to ↑-spins for both La and Ni in Fig. 3. The data for ↓-spins do not yield anything qualitatively distinct. We have checked that the spectral weight continues to be zero at EP. This confirms the correlated metallic behaviour of LaNiO2, which is in good agreement with the previously reported results for nickelates [5,9,11,35]. Even at much larger values of U1 (and U2), the system retains its metallic character. Even till as high as U1 = 10 eV, there is no trace of any insulating behaviour that emerges from our calculation.

To further support of the metallic state, we plot the temperature dependence of the dc resistivity defined by ρ = T∂ρ/∂T, where ρ(ω) is the optical conductivity, which has the form of

\[
σ(ω) \propto \frac{1}{ω} \int_{-∞}^{∞} dε \rho_0(ε) J(ω) D_ε(ω') D_ε(ω + ω)
\]

\[
\frac{[n_f(ω') - n_f(ω + ω)]}{[1 - n_f(ω + ω)]}
\]

\[
\text{(7)}
\]

ρ0(ε) is the non-interacting DOS and the spectral function is obtained via Eq. 4. For the strongly correlated materials, dc resistivity can be calculated using the relation of ρ. The parameters used in our calculation are U1 = 4.0 eV and U2 = 2.6 eV and we have the resistivity behaviour from a very low temperature all the way up to the room temperature. We have found that the total resistivity arising out of the contributions from both the bands (↑- and ↓-spin bands) follow a T2 behaviour. Since both the bands overlap with each other, we have only represented the resistivity data for ↑-spin only. Here the resistivity is normalized with respect to its maximum value. This type of metallic nature of LaNiO2 is consistent with the previously reported data on LaNiO2 [5,12]. It is further worthwhile to mention that the dc resistivity data presented in Fig. 4, although comprises of the total contribution from both the La and the Ni bands, the contribution from Ni, that is from the 3d band of Ni is the most dominant one.

In a recent study of the orbital-resolved spin susceptibility for NdNiO2 [36], the importance of the inter-orbital contribution was highlighted. The authors have found that the relative contributions to the susceptibility from the axial s-orbital of Ni to that from its d-orbital to be only 10%, while the same for the inter-orbital (s − d) contribution to the d-orbital is 20%. In comparison, the same for LaNiO2 only 1% and 5%, respectively. This confirms the total susceptibility in LaNiO2 is almost dominated by the d-orbital contribution [36].

Next, we present the magnetization plot of LaNiO2, where the spin-↑ and the spin-↓ states are partially filled with an occupation difference between them, thereby resulting in a net magnetic moment. To compute magnetization, we apply a magnetic field H and hence calculate the Green’s function. This yields the change in the density of state (DOS) induced by H. Finally, we evaluate the magnetization using,

\[
m = n_{i\uparrow} - n_{i\downarrow}
\]

\[
\text{(8)}
\]
LaNiO$_2$, namely, a nonmagnetic (NM), a ferromagnetic (FM) and an antiferromagnetic (AFM) states. Furthermore, we have obtained the energy difference between the AFM and FM states (\(\Delta E = E_{\text{AFM}} - E_{\text{FM}}\)) as a function of interaction energy, \(U\) (see Fig. 5). We observe that below \(U \approx 3.4\) eV the AFM state corresponds the lowest energy state and hence is more stable than the FM state by approximately 0.03 eV. However, when the interaction energy exceeds 3.4 eV, the FM state becomes more stable with an energy difference of approximately 0.28 eV. As long as the interaction energy is increased the system stays in the FM state with a value for the magnetic moment to be 0.28 \(\mu_B\). Figure 6 shows the magnetization, \(m\) vs the applied magnetic field, \(H\) curve. From the plot, it is clear that \(m\) shows a linear behaviour with \(H\) in the range shown in Fig. 6. This result is in contrast with the previously reported result of Refs. [11,37,38]. Where for RNiO$_2$ (R = Nd, La), they have found a stable C-type antiferromagnetic (AFM) ground state with magnetic moments inside the Ni spheres having an approximate value of 0.7 \(\mu_B\). Additionally, we should note that no experimental evidence for an antiferromagnetic order has been reported for this kind of RNiO$_2$ nickelates. Furthermore, for LaNiO$_2$, the susceptibility looks Pauli-like, except for an upturn in the low-temperature regime [4]. However, in Ref. [11] they have reported a ferromagnetic state which gives rise to a reduced magnetic moment of \(\sim 0.2 \mu_B\) at the GGA level, which is less stable than the C-type AFM state by 0.72 meV/Ni. The reason behind the discrepancy arises, because they have considered a non-interacting ground state, whereas we have considered strong electronic correlations. Also the linear dependence of the magnetization as a function of the external field for undoped LaNiO$_2$ shows widely different behaviour from the corresponding data for cuprates which show insulating long-range antiferromagnetic order in their undoped ground state.

Finally, the angle-resolved photoemission spectroscopy (ARPES) spectra can be considered as a helpful technique to support our results for the metallic ground state of LaNiO$_2$. Detailed ARPES studies on LaNiO$_2$ are not available in literature. The ARPES spectral intensity \(I(k, \omega)\) is given by, \(I(k, \omega) = I^0(k)A(k, \omega)f(\omega)\) where \(A(k, \omega)\) represents the spectral function, \(I^0(k)\) incorporates the dipole matrix elements, and \(f(\omega)\) is the Fermi distribution function. In the case corresponding to a momentum independent self-energy, the spectral intensity takes a form [39]

\[
I(k, \omega) \propto \frac{\text{Im} \Sigma(\omega)}{|\omega - \epsilon_k - \text{Re} \Sigma(\omega)|^2 + |\text{Im} \Sigma(\omega)|^2} f(\omega),
\]

where \(\epsilon_k\) is the noninteracting dispersion. \(\text{Im} \Sigma(\omega)\) and \(\text{Re} \Sigma(\omega)\) represent the imaginary and real parts of the self-energy, respectively. Figure 6 illustrates the photoemission intensity energy distribution curves (EDC) along \(\Gamma - X - M - \Gamma\) direction for the Ni \(\uparrow\)- and \(\downarrow\)-spin bands at a temperature \(T = 50\) K. Figure 6a, b shows the DMFT single particle spectral function at \(T = 50\) K for the Ni \(\uparrow\)- and the Ni \(\downarrow\)-spin bands, respectively. The presence of sharp quasiparticle peaks in the ARPES intensity confirm the Fermi liquid nature of the parent compound LaNiO$_2$.

We would like to make several remarks here. From our DFT plus DMFT calculations, we show that the normal state of the parent LaNiO$_2$ is quite different from its copper oxide counterpart. The ground state of LaNiO$_2$ is in a strongly correlated metallic state, which agreed and also have conflicts with some previously reported data. We have also identified the Ni-3d \((3d_{x^2-y^2})\) orbital as the most correlated one. The
metallic nature was confirmed by the $\text{Im} \Sigma(\omega)$ data and also $\text{LaNiO}_2$ shows a $T^2$ behaviour in the resistivity vs temperature plot. Furthermore, $\text{LaNiO}_2$ follows a linear dependence of magnetization, that is a ferromagnetic behaviour upon applying an external magnetic field. The magnetic ordering of the parent nickelate $\text{LaNiO}_2$ is quite different from the magnetic ordering of cuprates. In addition, in support of our Fermi liquid ground state, we also provide the ARPES data. The sharp quasiparticle peaks in ARPES intensity confirm the presence of a FL ground state.

**Author contributions**

All authors have equally contributed to the manuscript.

**Data Availability Statement** This manuscript has associated data in a data repository. [Authors’ comment: The data described in this manuscript are available from Mijanur Islam on request.]

**References**

1. D. Li et al., *Nature* **572**, 624627 (2019)
2. T. Siegrist, S.M. Zahurak, D.W. Murphy, R.S. Roth, *Nature* **334**, 231232 (1988)
3. M. Crespin, P. Levitz, L. Gatineau, J. Chem. Soc. Faraday Trans. **79**, 1181 (1983)
4. M.A. Hayward, M.A. Green, M.J. Rosseinsky, J. Sloan, J. Am. Chem. Soc. **121**, 8843 (1999)
5. A. Ikeda, Y. Krockenberger, H. Irie, M. Naito, H. Yamamoto, *Appl. Phys. Exp.* **9**, 061101 (2016)
6. A.S. Botana, M.R. Norman, *Phys. Rev. Mat.* **2**, 10480 (2018)
7. B. X. Wang, H. Zheng, E. Krivyakina, O. Chmaissem, P. P. Lopes, J. W. Lynn, L. C. Gallington, Y. Ren, S. Rosenkranz, J. F. Mitchell, D. Phelan (2006). arXiv preprint arXiv:2006.09548
8. V.I. Anisimov, D. Bukhvalov, T.M. Rice, *Phys. Rev. B* **59**, 7901 (1999)
9. K.W. Lee, W.E. Pickett, *Phys. Rev. B* **70**, 165109 (2004)
10. T. Liu, H. Wu, T. Jia, X. Zhang, Z. Zeng, H.Q. Lin, X.G. Li, *AIP Adv.* **4**, 047132 (2014)
11. A.S. Botana, M.R. Norman, *Phys. Rev. X* **10**, 011024 (2020)
12. D. Kaneko, K. Yamagishi, A. Tsukada, T. Manabe, M. Naito, *Phys. C Supercond.* **469**, 936–939 (2009)
13. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
14. G. Kresse, J. Furthmüller, J. *Phys. Rev. B* **54**, 11169 (1996)
15. H. Sakakibara, H. Usui, K. Suzuki, T. Kotani, H. Aoki, K. Kuroki (2019). arXiv preprint arXiv:1909.00060
16. Nomura Y, Hirayama M, Tadano T, Yoshimoto Y, Nakamura K, Arita R (2019). arXiv preprint arXiv:1909.03942
17. M. Jarrell, *Phys. Rev. Lett.* **69**, 168 (1992)
18. M. Rozenberg, X.Y. Zhang, G. Kotliar, *Phys. Rev. Lett.* **69**, 1236 (1991)
19. A. Georges, W. Krauth, *Phys. Rev. Lett.* **69**, 1240 (1992)
20. M. Jarrell, T. Pruschke, Z. *Phys. B* **90**, 187 (1996)
21. M. Caffarel, W. Krauth, *Phys. Rev. Lett.* **72**, 1545 (1994)
22. Q. Si, M. Rozenberg, G. Kotliar, A. Ruckenstein, *Phys. Rev. Lett.* **72**, 2761 (1994)
23. H. F. Fotso, K. M. Tam, J. Moreno (2011). arXiv preprint arXiv:2011.05522
24. A. Georges, G. Kotliar, W. Krauth, M.J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996)
25. S. Koley, *Solid State Com.* **251**, 23–27 (2017)
26. S. Koley, M.S. Laad, N.S. Vidhyadhiraja, A. Taraphder, *Phys. Rev. B* **90**, 115146 (2014)
27. N. Dasari, W.R. Mondal, P. Zhang, J. Moreno, M. Jarrell, N.S. Vidhyadhiraja, *Euro. Phys. J. B* **89**, 202 (2016)
28. A. Garg, H.R. Krishnamurthy, M. Randeria, *Phys. Rev. B* **72**, 024517 (2005)
29. S. Koley, N. Mohanta, A. Taraphder, J. *Phys. Cond. Mat.* **27**, 185601 (2015)
30. M.S. Laad, L. Craco, E. Müller-Hartmann, *Phys. Rev. Lett.* **91**, 156402 (2003)
31. A. Georges, G. Kotliar, *Phys. Rev. B* **45**, 6479 (1992)
32. H. Kajueter, Ph.D. thesis, Rutgers University, New Brunswick (1996)
33. J.M. Luttinger, J.C. Ward, *Phys. Rev.* **118**, 1417 (1960)
34. D.C. Langreth, *Phys. Rev. Lett.* **150**, 516 (1966)
35. A. Ikeda, T. Manabe, M. Naito, Phys. C Supercond. **495**, 134–140 (2013)
36. P. Adhikary, S. Bandyopadhyay, T. Das, I. Dasgupta, T. Saha-Dasgupta, *Phys. Rev. B* **102**, 100501 (2020)
37. Y. Wang, C.-J. Kang, H. Miao, G. Kotliar, *Phys. Rev. B* **102**, 161118(R) (2020)
38. R. Zhang, C. Lane, B. Singh, J. Nokelainen, B. Barbelliini, R.S. Markiewicz, A. Bansil, J. Sun. *Comm. Phys.* **4**, 118 (2021)
39. S. LaShell, E. Jensen, T. Balasubramanian, *Phys. Rev. B* **61**, 2371 (2000)