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 $\text{La}_{\{3\}}\text{Ni}_{\{2\}}\text{O}_{\{6\}}$ and trilayer $\text{La}_{\{4\}}\text{Ni}_{\{3\}}\text{O}_{\{8\}}$
nickelates from first principles

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Electronic and Magnetic Structure of Bi-layer, $\text{La}_3\text{Ni}_2\text{O}_6$ and Tri-layer, $\text{La}_4\text{Ni}_3\text{O}_8$ Nickelates

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We revisit the electronic and magnetic structure of bi-layer, $\text{La}_3\text{Ni}_2\text{O}_6$ and tri-layer, $\text{La}_4\text{Ni}_3\text{O}_8$ nickelates, in terms of detailed first-principles calculations. Through construction of an axial orbital, we show that the crystal field splitting obtained in a single layer case, is modified substantially in the multi-layer case leading to a near degeneracy of several levels and a possible bi-stability between low spin and high spin state of Ni in specific cases. The issue needs to be settled by further experimental studies, followed by theoretical investigations.

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Following the success of cuprates in high T_c superconductivity, attention has been focused on layered materials¹, such as Ni based compounds.² Ni is next to Cu in the periodic table, and if it can be realized in the $1+$ oxidation state, may have a similar electronic structure as Cu^{2+} . However, Ni^{1+} oxides, are generally found to be chemically unstable. The recent reports^{3,4} in synthesizing $\text{La}_3\text{Ni}_2\text{O}_6$ (2-LNO) and $\text{La}_4\text{Ni}_3\text{O}_8$ (3-LNO) with square planar co-ordination of Ni by O, as in CuO_2 , therefore, have generated much interest. Both 2-LNO and 3-LNO, containing a bi-layer and tri-layer of NiO_2 planes respectively, crystallize in $I4/mmm$ space group, as shown in Fig.1(a). Both compounds have been investigated experimentally and by first-principles calculations.⁴⁻⁸ However, issues like the ground state magnetic structure, the spin state of Ni, the genesis of band structure in terms of hybridization of different degrees of freedom, remain debated.

In this communication, we revisit the electronic and magnetic structure of both compounds, in terms of detailed density functional theory (DFT) study, using the plane wave based basis as implemented in

the VASP code⁹ and the muffin-tin orbital (MTO) based linear MTO (LMTO) and N-th order MTO (NMTO) methods.^{10,11} The exchange correlation functional was chosen to be Generalized Gradient Approximation (GGA).¹² The missing correlation beyond GGA at Ni sites, was taken into account through GGA+U calculation. For the plane wave calculations, we used projector augmented wave (PAW) potentials,^{13,14} and the wave functions were expanded in the plane wave basis with a kinetic energy cutoff of 600 eV. Reciprocal space integrations were carried out with a k mesh of $8 \times 8 \times 6$. The GGA+U calculations were performed with the +U implementation of Dudarev *et al.*¹⁵

Fig. 1(b) shows the basic, non spin-polarized band structure of 2-LNO and 3-LNO. As is seen, for 2-LNO the conduction band, crossing the Fermi level, E_F (set at zero in the figure) and spanning an energy range of about -1eV to 2 eV, is dominantly of $\text{Ni } d_{x^2-y^2}$ character. The $\text{Ni } d_{xy}$, d_{xz} , d_{yz} and d_{z^2} dominated bands all lie within a energy range of about -2 eV to -0.5 eV. The states below ≈ -2 eV, are of dominant O- p characters. The large bi-layer splitting (bonding-antibonding splitting due to interlayer coupling) between d_{z^2} dominated bands is evident. The k -dependent bi-layer splitting among $\text{Ni } d_{x^2-y^2}$ dominated bands is also seen, which vanishes at the Γ point and is maximum at the saddle point, as found in cuprates.¹⁶ The basic features of the electronic structure of 3-LNO is similar to that of 2-LNO, barring a few important differences. The interlayer splitting of d_{z^2} dominated bands is larger in case of 3-LNO, due to addition of one extra layer, which splits bands into bonding, antibonding and nonbonding combinations. This results in the d_{z^2} dominated, antibonding band to be pushed closer to $\text{Ni } d_{x^2-y^2}$ bands, compared to 2-LNO. The O- p dominant bands, on the other hand, are pushed down compared to bi-layer.

In the next step, we introduced spin polarization and studied four different magnetic structure of Ni spins in a $\sqrt{2} \times \sqrt{2} \times 1$ supercell, (i) ferromagnetic (FM), (ii) A-type antiferromagnetic (AFM) which involves parallel (antiparallel) alignments within (between) the layers, (AFM-A), (iii) C-type AFM which involves antipar-

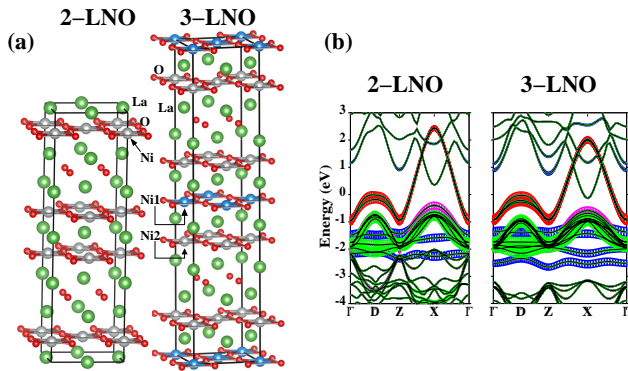


FIG. 1: (a) Crystal structures of 2-LNO and 3-LNO. (b) Non spin-polarized band structure of 2-LNO and 3-LNO. The bands are projected onto $\text{Ni } d_{x^2-y^2}$ (red), d_{z^2} (blue), d_{xy} (green) and degenerate d_{xz} , d_{yz} (magenta) characters.

TABLE I: Total moment (per Ni atom), individual Ni moments, and the total energies of various magnetic arrangements of Ni spins (ΔE), measured from the lowest energy state.

		Total Mom. (μ_B)	Ni moment (μ_B)	$\Delta E/Ni$ (meV)
2-LNO	FM	0.50	0.63	0
	AFM-A	0.0	-0.64/0.64	0.72
	AFM-C (HS)	0.0	-1.26/1.25	325
	AFM-C (LS)	0.0	-0.61/0.61	265
	AFM-G (HS)	0.0	-1.29/1.22	325
	AFM-G (LS)	0.0	-0.59/0.59	276
3-LNO	FM	0.67	0.76	0.48
	AFM-A	0.22	0.78/-0.78	0
			-0.76/0.76	
	AFM-C (HS)	0.0	-1.41/1.41	77
			-1.22/1.22	
	AFM-C (LS)	0.0	-0.87/0.87	215
			-0.86/0.86	
	AFM-G (HS)	0.01	-1.09/1.02	310
			-1.17/1.15	
	AFM-G (LS)	0.0	0.75/-0.74	245
			0.75/-0.74	
	SDW	0.04	0.81/-0.77/0.72	96
			-0.81/0.75/-0.72	
			-0.79/0.74/-0.73	

allel (parallel) alignments within (between) the layers, (AFM-C) and (iv) G-type AFM which involves antiparallel alignments in all directions (AFM-G). The calculated magnetic moments and the relative energetics of various magnetic configurations, as obtained in plane wave basis within GGA+U for a choice of $U = 6$ eV and $J = 1$ eV are summarized in Table I. The results do not depend on the choices of U and J values significantly. The double counting correction used for the calculations is that of fully localized limit (FLL). The spin state of Ni in these compounds have been a matter of discussion.^{17,18} Given the absence of apical oxygens in the planar co-ordination of oxygens surrounding the Ni atom, one would expect Ni to be in low spin (LS) state.^{3,4} We carried out the fixed moment calculations with the moment of Ni varied over a range in a FM configuration. In the absence of any appreciable charge disproportionation of Ni atoms, the nominal electron count of Ni in 2-LNO (3-LNO) is $d^{8.5}$ ($d^{8.67}$). This would lead to LS Ni moments of 0.5 (0.67) μ_B for 2-LNO (3-LNO), the corresponding high spin (HS) moments being 1.5 (1.33) μ_B . From the results, presented in Fig. 2, we find the LS to be more stable, compared to HS state by about 0.2 - 0.3 eV. The stabilization of LS configuration is in agreement with the results obtained in Refs.5,6, but in disagreement with the findings of Refs.7,8. A recent study¹⁷ pointed to different schemes of double counting correction for this discrep-

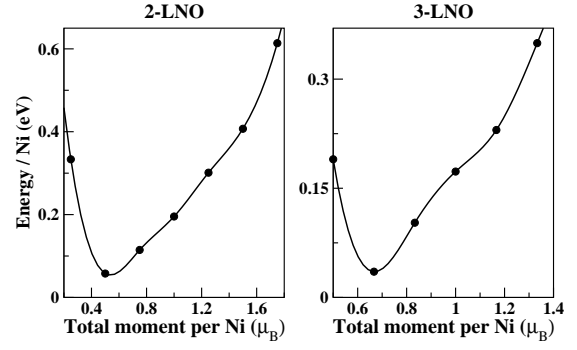


FIG. 2: Total energy plotted as a function of varying magnetic moment for 2-LNO and 3-LNO.

ancy. We find that even using FLL scheme, our calculations for FM spin arrangement predict stabilization of LS state rather the HS state. From Table I, we find that FM and AFM-A converge to LS state with Ni moments close to 0.5 (0.7) μ_B for 2-LNO (3-LNO). We failed to stabilize the HS states for FM and AFM-A configurations. The AFM-C and AFM-G, on the other hand, were found to either converge to LS state or HS state depending on the starting configurations, indicating a bi-stability with local minima at LS and HS states. The LS state for AFM-G and AFM-C is energetically more stable compared to HS, with the exception of AFM-C for 3-LNO.

The band structures of 2-LNO and 3-LNO for FM, AFM-A, AFM-C, AFM-G are shown in Figs 3 and 4, respectively. For FM/AFM-A, only majority spin channel is shown, as the states are either filled or empty in the other spin channel. Considering first 2-LNO, for the LS cases, we consistently find the solutions to be metallic with antibonding $Ni-d_{x^2-y^2} - O-p \sigma$ band crossing E_F , similar to the low energy orbital composition found in case of cuprates. For HS cases, on the other hand, the low-energy states are of dominant antibonding $Ni-d_{xy} - O-p \pi$ character. The ground state for HS, AFM-C structure turned out to be semiconducting. For the tri-layer case, for the LS cases, though the states are of primarily antibonding $Ni-d_{x^2-y^2} - O-p \sigma$ character, we find admixture of $Ni-d_{z^2}$ too, seen in terms of formation of a central lobe at the Ni site, which should have a node for pure $Ni-d_{x^2-y^2}$ character. For HS cases, the low energy states for AFM-G are of primarily antibonding $Ni-d_{xy} - O-p \pi$ character, while that of AFM-C type is curious with largely admixed $Ni-d_{z^2} - Ni-d_{x^2-y^2}$ states (cf insets in Figs 3 and 4).

Further, we carried out NMTO-downfolding calculations, in which, starting from an all orbital calculation, we kept active only the Ni- d orbital degrees of freedom and integrated out the rest.¹¹ Such calculations are expected to give rise to accurate estimates of the positions of various Ni- d levels. In the absence of any inter-layer coupling, the crystal field splitting of Ni- d levels at individual NiO_2 layers are shown in the extreme left hand or right hand sides in each panel of Fig. 5. For both

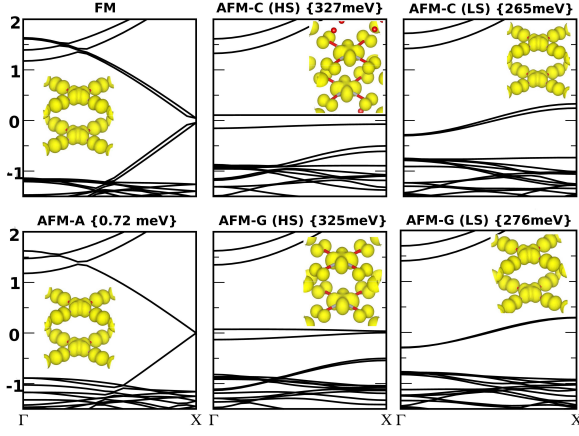


FIG. 3: (Color online) The band structures of 2-LNO. Insets show the charge density plots corresponding to low energy bands for each case. The numbers in the bracket in the heading indicate the total energy.

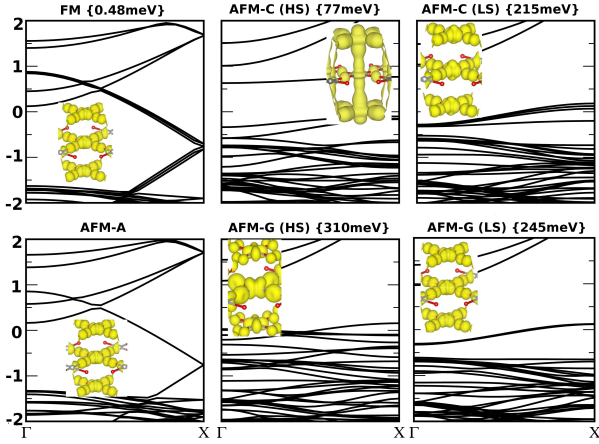


FIG. 4: (Color online) Same as in Fig. 3, but for 3-LNO.

compounds, we find that planar NiO_2 geometry leads to d_{z^2} level to be the lowest energy, followed by degenerate d_{xz} , d_{yz} and d_{xy} levels in increasing order of energy. The $d_{x^2-y^2}$ level is separated from the rest, by a separation of about 1.3-1.4 eV. This level diagram is similar to that in text book¹⁹ for a square planar geometry and different from that presented in recent Refs.7,8. The interlayer coupling is mediated by formation of an axial orbital, which is found to be a combination of Ni- s , Ni- d_{z^2} and O- p .²⁰ The interlayer coupling gets further strengthened by coupling with La -5 d characters, reflected in tails of the axial orbital, sitting at La sites intervening different layers, as shown in Fig. 5. The energy of the such a renormalized axial orbital is given by,

$$\epsilon_a = \epsilon_{z^2} + \frac{t_{z^2p}^2}{E_F - \epsilon_p} + \left(\frac{t_{sp} t_{z^2p}}{E_F - \epsilon_p} + t_{s,z^2} \right)^2 / \left(\epsilon_s - E_F + \frac{t_{sp}^2}{E_F - \epsilon_p} \right),$$

where ϵ_{z^2} , ϵ_p and ϵ_s are bare onsite energies of the Ni- d_{z^2} , O- p and Ni- s . t_{sp} (t_{z^2p}) indicates hopping between Ni- s (Ni- d_{z^2}) and O- p . The hybridization with La and O- p_z introduces an additional hopping interaction between

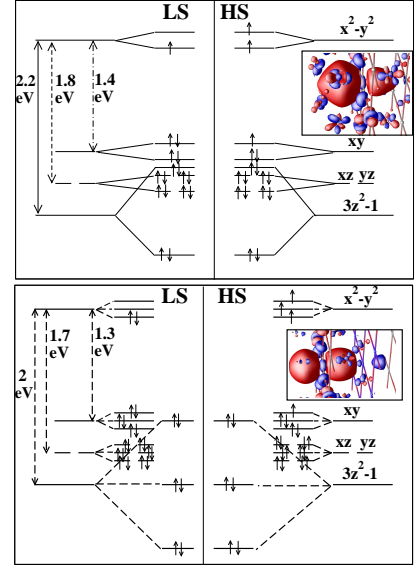


FIG. 5: (Color online) The positions of Ni- d energy levels and their occupancies for LS and HS cases, for 2-LNO (top panels) and 3-LNO (bottom panels). The insets in right panels show the plot of axial orbitals. Plotted are the constant value surfaces.

Ni- s and Ni- d_{z^2} , expressed as t_{s,z^2} .

This mixing with Ni- s as well as O- p and La- d strongly renormalizes the Ni- d_{z^2} level, which splits into bonding and anti-bonding levels for 2-LNO and into bonding, non-bonding and anti-bonding levels for 3-LNO. The resulting interlayer splitting for the renormalized Ni- d_{z^2} level, the axial level, is maximum within all the d levels, with the separation between lowest bonding level and highest anti-bonding level to be about 0.8 (1.4) eV for 2-LNO (3-LNO). The interlayer splitting of $d_{x^2-y^2}$, d_{xz} , d_{yz} , d_{xy} are small, of the order of 0.2 -0.3 eV, arising due to finite mixing with the axial orbital. This causes the renormalized, anti-bonding Ni- d_{z^2} level to be pushed significantly higher up, positioning it just below (degenerate with) the d_{xy} levels for 2-LNO (3-LNO), as shown in Fig. 5. For understanding the results presented in Figs. 3 and 4, one further needs to add the bandwidth effect, which crucially depend on the alignments of neighboring Ni spins - FM alignments resulting larger bandwidths compared to AFM alignments. Considering 2-LNO, the population of levels in LS situation leads to the situation that all states except $d_{x^2-y^2}$ are occupied in both spin channels. $d_{x^2-y^2}$ is occupied by one, unpaired electron, causing it to be the low energy state. This leads to a metallic state due to the large bandwidth of Ni- $d_{x^2-y^2}$ - O- p σ bonding and relatively small interlayer splitting of $d_{x^2-y^2}$ states. The population of levels in the HS situation, on the other hand, leads to the situation where all states are occupied in the majority spin channel, and in the minority spin channel bonding d_{xy} state to be the highest occupied state. The small bandwidth offered by Ni- d_{xy} - O- p π bonding in the AFM configuration then may lead to a

semiconducting solution with a gap formed between occupied, bonding d_{xy} state and unoccupied, antibonding d_{xy} state, as found for the AFM-C case (cf Fig.3). For 3-LNO, while for LS cases, the highest occupied state is bonding $d_{x^2-y^2}$ state, giving rise to metallic solutions, the HS cases are delicate due to near degeneracy between anti-bonding d_{z^2} and d_{xy} levels. Depending on the bandwidths which is dictated by the details of the magnetic arrangements, one or the other forms the low energy band (d_{xy} for AFM-G and d_{z^2} for AFM-C). Also, the band structure effect causes the $d_{x^2-y^2}$ and renormalized d_{z^2} states to hybridize strongly, which are energetically now separated by about 1 eV compared to ≈ 2 eV for the single layer situation. Finally, for $\text{La}_4\text{Ni}_3\text{O}_8$ an AFM-spin density wave (SDW) solution was proposed in Ref.6 based on nesting of Fermi surface. We have also checked the possibility of this solution in our calculation. The calculated total energy per Ni turned out to be 96 meV/Ni (see Table I), placing AFM-SDW solution in close competition to AFM-C HS solution.

In summary, we have carried out detailed electronic structure calculations of $\text{La}_3\text{Ni}_2\text{O}_6$ and $\text{La}_4\text{Ni}_3\text{O}_8$ which have been discussed in recent literature.^{3-8,17,18} Our calculations show, that the crystal field splitting obtained for a single layer planar geometry is modified substantially in the multi-layer case causing a near degeneracy of several levels. The interlayer coupling in multi-layer case, is assisted by an axial orbital, constructed out of $\text{Ni-}d_{z^2}\text{-Ni-s-O-}p$ and interestingly, of $\text{La-}d$. Our calculation show, for both compounds, FM or AFM-A type configuration to be the magnetic ground state (GS), with near degeneracy of the two states. The solutions for FM or AFM-A type configuration turn out to be metallic. We find the LS states to be energetically more stable for the FM and AFM-A configurations. For AFM-C and AFM-G, we find convergence is achieved either in LS state or in HS state depending on the starting configuration. This leads to bi-stability, present for the AFM structures of these compounds and may explain the apparent discrepancies between different DFT results.^{6-8,17} For example, the AFM-C type was investigated in Ref.6, however, since the starting configuration was assumed to be that of LS, the convergence only to LS state was achieved (which is energetically ≈ 200 meV higher than the GS), thereby missing out the energetically comparable state of AFM-C(HS) to that of AFM-SDW. The energetics of different magnetic structures were not reported in Ref.7, the starting configurations were also not discussed. Since both Refs.6 and 7 used the same basis set and same computer package (WIEN2k) one would expect similar results to be obtained, which however may be influenced by the starting configuration, as our study reveals.

At the end, the situation needs to be clarified in terms of further experimental studies. The experiments carried out on polycrystalline samples indicate thermally activated conducting properties, for both compounds, while the minimum energy states given by DFT are found to be metallic. However, the experimental transport proper-

ties may be dominated by poor percolation in the loosely packed powder pellet, or dominated by semiconducting behavior along the perpendicular to layer direction. Unfortunately, so far, the single crystals seem impossible to obtain.⁶ For 2-LNO, no magnetic ordering has been found⁵ down to 4 K while for 3-LNO, recent neutron diffraction¹⁸ also finds no signature of magnetic reflection at low T. Energetics presented in Table I, show both AFM-C (HS) configuration and SDW to be energetically comparable, and intermediate in energy between AFM-A/FM and the high energy structures like AFM-G (LS and HS) or AFM-C(LS). It might be possible that either AFM-C (HS) or SDW state is the state obtained experimentally, as a total moment of $0.22 \mu_B$ obtained for AFM-A (the GS according to present calculation) is not seen experimentally (cf Fig. S2 in Ref.6). We need to remember though, AFM-C (HS) and SDW state gives rise to two different conducting properties. AFM-C(HS) is insulating, while SDW is metallic [cf. density of states (DOS) presented in Ref.6]. It is worth mentioning at this point that the NMR data which is a reliable probe for the DOS shows a Korringa term in the low temperature phase. While the NMR shows a sizable reduction of the DOS at low temperature however it is important to note that the suppression of the DOS is not complete. Therefore, to resolve the puzzles, one surely needs a reliable experimental way to extract the charge transfer gap of the parent compound, which to date is not available.

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