The driving force for charge ordering in rare earth nickelates

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Abstract

We show that charge ordering (more precisely, two-sublattice bond disproportionation) in the rare earth nickelate perovskites is intimately related to a negative charge transfer energy. By adding an additional potential on the Ni d states we are able to vary the charge transfer energy and compute relaxed structures within an ab-initio framework. We show that the difference in Ni-O bond lengths and the value of the ordered state magnetic moment correlate with the charge transfer energy and that the transition to the bond-disproportionated state occurs when the effective charge transfer energy becomes negative.
Although the 3d transition metal oxides have been studied since the 1950’s, improved growth and characterization techniques as well as new theoretical approaches have continued to yield new insights. The rare earth perovskite nickelates are of particular current interest. These materials exhibit metal-insulator transitions for all members of the family RENiO$_3$ (where RE denotes a rare earth ion), with the exception of RE = La. The metal-insulator transition is coincident with a crystal distortion in which the mean Ni-O bond length alternates between two inequivalent Ni sites, defining a bond disproportionation. This state is sometimes also referred to as “charge ordered”.

While the rare earth perovskite nickelates exhibit bond disproportionation, the rare earth perovskite cobaltates formed with the neighbouring transition metal atom Co in the same oxidation state exhibit no such ordering. An important parameter that controls the electronic structure for the late transition metal oxides is the charge transfer energy, given by the energy required to transfer an electron from the oxygen p levels to the transition metal d levels. The charge transfer energy decreases as one goes across the 3d transition metal series from Ti to Cu and it is natural to associate the change in charge transfer energy with the propensity to bond disproportionation.

Formal valence considerations assign the d$^7$ configuration to the Ni in the RENiO$_3$ perovskites. However, if the charge transfer energy is strongly negative, the electronic configuration is more appropriately represented as d$^8\bar{L}$ (with the \( \bar{L} \) denoting a hole on the ligand). The importance of an effectively negative charge transfer energy in this family of compounds was first pointed out by Barman et al. while discussing the insulating ground state of NdNiO$_3$ in contrast to the metallic one of LaNiO$_3$. Mizokawa et al. carried out model Hamiltonian calculations for a multiband Hubbard model and could capture the bond disproportionation at a negative value of the charge transfer energy when they included a breathing mode distortion of the NiO$_6$ octahedra. This suggests that the combination of lattice distortions and a negative charge transfer energy drove the charge ordering. Mazin and coworkers argued that part of the energy lowering associated with the disproportionation came from the energy gain from Hund’s intra atomic exchange interactions, which favor a high-spin d$^8$ state. Building on the Mizokawa picture, Park, Millis and Marianetti presented density functional plus dynamical mean field calculations that explained the disproportion in terms of a site selective Mott transition occurring in a situation in which the charge transfer energy was very negative, and Johnson and collaborators later consid-
ered the same physics in a model system perspective \cite{17}. On the other hand, Peil and Georges \cite{18} argued that an appropriate low energy description of the physics was in terms of a Hubbard model with a vanishing or negative U; in this effective low energy picture the bond-disproportionated state is indeed characterized by charge order.

In this paper we take a new approach to this issue by examining in more detail the connection between bond disproportionation and the charge transfer energy. Introducing a potential on the Ni d states, we are able to vary the charge transfer energy and examine the ensuing changes in the structure as well as the electronic structure within an \textit{ab initio} framework in contrast to all model Hamiltonian approaches in the past. We find that the onset of charge ordering is characterised by the point at which the Ni $d$ band enters the oxygen $p$ band, defining the effective negative charge transfer energy\cite{19, 20}. This destabilizes the RE-oxygen network which is otherwise ionic, driving the charge ordering.

The electronic structure of NdNiO$_3$ was calculated within a projected augmented wave\cite{21} implementation of density functional theory within the Vienna \textit{ab initio} simulation package (VASP)\cite{22, 23} code. The experimental lattice parameters were taken\cite{24}. The magnetic structure (both T-AFM, non-collinear E'-AFM and FM) was imposed and the electronic structure was calculated within the Dudarev implementation\cite{25} of GGA+U with a U of 4 eV on the Ni sites. The generalized gradient approximation\cite{26} was used for the exchange correlation functional. A k-points grid of 4x6x2 was used for calculating the electronic structure. While the lattice parameters were kept fixed at the experimental values, the internal positions were optimised to find the minimum energy configuration so that the forces were less than $10^{-3}$ eV/Å. The general features of the structure are similar when we assume ferromagnetic order. Consequently the rest of the analysis in terms of microscopic model has been carried out for the ferromagnetic unit cell which is smaller. A k-point mesh of 6x4x6 and an energy cutoff of 500 eV was used. Spheres of radii 1 Å are constructed around each atom for the calculation of the density of states and magnetic moment and within the spheres centered on the Ni ions a d-symmetry potential of constant radial part is introduced. The structure is then optimised to find the structural and magnetic parameters in the presence of the potential and the charge transfer energy is quantified by using maximally localized wannier function methods\cite{27, 29} to map the ab-initio band structure onto a tight binding model using the VASP to Wannier90 interface \cite{30}. The results are used to construct a schematic diagram of the electronic structure.
There are two candidate orderings which have been proposed for the magnetic structure of the magnetic nickelates. The first corresponds to an up-up-down-down ordering of the spins on the Ni along the three pseudo cubic directions, and has been referred to as T-AFM type magnetic structure [31]. There are variants that differ slightly in the stacking of these chains, and differ slightly in the total energy [32]. The other structure corresponds to a non-collinear one in which the neighbouring spins have equal magnitude but are rotated by $90^\circ$. We have used both of these structures to initialize our calculations; we find that both cases relax to the same magnetic configuration. The fully relaxed structure contains Ni-O$_6$ octahedra of short mean bond length ($\sim 1.90$ Å for the case with no extra Ni potential applied) and NiO$_6$ octahedra of longer mean bond length ($\sim 2.0$ Å if no Ni potential is applied). The Ni sites with short-bond octahedra have a zero magnetic moment, while the Ni sites with long-bond octahedra have a magnetic moment of $1.50\ \mu_B$ (Ni$^{2+}$). A similar difference of moment was found experimentally and was initially interpreted as a Ni charge disproportionation [8]. However, examining the density of states associated with each of the Ni sites (Fig. 1), we find that the $t_{2g}$ states on both Ni sites are completely filled, while the mean occupancy of the $e_g$ states on both sites is $\sim 2$. On the long-bond Ni site the majority spin $e_g$ channel is found deep inside the valence band and is fully occupied, while the minority spin $e_g$ channel is empty, with a very small admixture of O $p$ implying an Ni $d^8$ configuration. On the short-bond Ni sites the high-lying $e_g$ states are found at $\sim 1-2$ eV in the conduction band and have significant O $p$ admixture; these are antibonding states; the corresponding bonding states are located deep inside the valence band. The significant O $p$ admixture suggests that one should associate an electronic configuration of $d^8\Sigma^2$ as previously suggested [14, 16, 17]. As discussed by Park et al [16] the spin splitting of these states is very small (zero in the present calculation), indicating that the holes on the oxygen states form a singlet with the Ni $e_g$ electrons which accounts for the zero magnetic moment.

Having established that the DFT+U calculations correctly reproduce the basic physics of NdNiO$_3$, we analyse the consequences of varying the charge transfer energy. For convenience in the analysis and interpretation we consider a ferromagnetic ground state (which can also be stabilized in the DFT+U method, although it is not the true ground state). In the ferromagnetic state the inequivalent Ni sites have respectively a large and a small moment, but in contrast to the T-antiferro state the smaller moment, while much less than the larger
FIG. 1. The spin resolved (upper and lower panel) Ni \( e_g \) and O \( p \) contributions to the density of states for (a) Ni\(^{2+}\), (b) Ni\(^{4+}\) sites in NdNiO\(_3\) considering the T-type antiferromagnetic structure and \( U=4 \) eV on Ni.

one, is not zero. We vary the potential acting on the Ni, and for each value of the potential determine the on-site magnetic moments, the amplitude of the bond disproportionation, and the charge transfer energy as defined from the Wannier fit.

Because the charge transfer energy is a monotonic function of the on-site potential, we plot the magnetic moments and mean octahedral bond lengths against charge transfer energy \( \Delta \) in Fig. 3. As \( \Delta \) is increased from the value \( \approx -1.15 \) eV, Fig. 3a shows that the mean bond length of the short-bond octahedra increases, while the mean bond length of the long-bond octahedra changes only slightly. For charge transfer energies greater than about 1 eV the difference between the two mean octahedral bond lengths becomes negligible. Fig 3b shows a similar increase in the magnetic moment of the short-bond site as the charge transfer
energy is increased, with the difference in moments between sites becoming negligible for $\Delta \gtrsim 1 \text{ eV}$.

Having established that the charge transfer energy controls the disproportionation physics, we now consider in more detail the mechanism. We have calculated the width of the oxygen $p$-band within the tight-binding model by switching off the $p$-$d$ interactions. We find that the disproportionation disappears when the charge transfer energy become large enough that the $p$-band becomes filled, as shown schematically in Fig. 4. This supports the view [16] that the disproportionation arises from a preferential hybridization of the ligand holes with one of the Ni states.

Future work will examine trends across the nickelate series from this point of view, and will consider the relation between the charge transfer energy and the effective $U$ of the low energy theory introduced by Subedi, Peil and Georges [18].

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FIG. 3. Variation in the (a) Ni-O bondlengths and (b) Magnetic moments on the Ni sites with $\Delta$.

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FIG. 4. Schematic indicating the definitions $\Delta$ and $\Delta_{eff}$ used in the text. While a positive $\Delta_{eff}$ has uniform NiO$_6$ octahedra, a negative $\Delta_{eff}$ leads to transfer of holes to the oxygen p bands and occurrence of a breathing distortion of the NiO$_6$ octahedra.

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