Quantum Confinement Induced Molecular Correlated Insulating State in $La_4Ni_3O_8$

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The recently synthesized layered nickelate $La_4Ni_3O_8$, with its cupratelike NiO_2 layers, seemingly requires a Ni1 (d^8) + 2Ni2 (d^9) charge order, together with strong correlation effects, to account for its insulating behavior. Using density functional methods including strong intra-atomic repulsion (Hubbard U), we obtain an insulating state via a new mechanism: *without charge order*, correlated (Mott) insulating behavior arises based on quantum-coupled, spin-aligned molecular Ni2-Ni1-Ni2 d_{z^2} trimer states across the trilayer (molecular rather than atomic states), with antiferromagnetic ordering within layers. The weak and frustrated magnetic coupling between cells may account for the small spin entropy that is removed at the Néel transition at 105 K and the lack of any diffraction peak at the Néel point.

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Nearly 25 years since the discovery of high temperature superconductivity (HTS), the question persists: why does HTS occur only in copper oxides and not other layered oxides? Nickelates with cupratelike structures [1] have seemed to be the most likely candidates: the Cu^{2+} d^9 configuration with active $d_{x^2-y^2}$ orbital maps onto the Ni^{1+} configuration, but this is known to be a problematic charge state. Nevertheless, difficult charge states may sometimes be stabilized, such as the nominal Ni^{1+} (“infinite-layer”) compound $LaNiO_2$ prepared by topotactic exchange of oxygen [2]. Cupratelike electronic structures in other oxides have been pursued since soon after HTSs were discovered. The charge conjugate analog Sr_2VO_4 (d^1 vs d^9) presented hope [3,4] and displays magnetic and orbital ordering [5] but has never shown superconductivity. Layered nickelates have been seen as the best mimic of HTS if the d^9 Ni^{1+} charge state can be stabilized, and theoretical interpretation of the few known prospects has begun [6,7]. The $LaNiO_3/LaAlO_3$ superlattice proposed by Khaliullin and collaborators [8,9] is an example that has been suggested to produce an HTS-like Fermi surface, but is based on the more common Ni^{3+} ion and has not yet produced superconductivity.

The discovery by Greenblatt’s group of a Ruddlesden-Popper sequence [10] of phases $La_{n+1}Ni_nO_{2n+2}$ with n cupratelike NiO_2 layers has reinvigorated interest in nickelates, with a focus on $La_4Ni_3O_8$ (“La438”) where stoichiometry is attained [11,12]. In an ionic picture, the mean Ni valence in $La_{n+1}Ni_nO_{2n+2}$ is $+(n+1)/n$, i.e., metallic. However, La438 is highly insulating[13], with a room temperature resistivity $\sim 10^3\ \Omega$ cm increasing by 6 orders of magnitude down to 25 K. Magnetic ordering is observed [13] at $T_N = 105$ K, with NMR data indicating an antiferromagnetic (AFM) transition [14]. The entropy loss at T_N is only $\frac{1}{3}R\ln 2$ per Ni, suggesting unconventional magnetic behavior in this system.

La438 crystallizes in a tetragonal unit cell, with space group $I4/mmm$ (#139) and lattice parameters $a = 3.9633$ Å, $c = 26.0373$ Å. The structure, pictured in Fig. 1, consists of three NiO_2 “infinite-layer” planes separated by layers of La^{3+} cations but no oxygen. On either side of this trilayer slab lies a fluorite $La/O_2/La$ layer, with the same structure as the corresponding layer in LaFeAsO. While in a sense isoelectronic with doped cuprates as it seems to involve some mix of Ni^{1+} and Ni^{2+} cations, the electronic and magnetic structure of the Ni ions is still unclear. As mentioned, the low oxidation state Ni^{1+} is enigmatic; to obtain such a configuration for Ni is not easy, and these Ruddlesden-Popper phases are unstable at moderate ($\sim 375\,^\circ$C) temperature [10] to decomposition into La_2O_3 and Ni metal. In the Ni^{1+} “infinite-layer” compound $LaNiO_2$ it was found to be impossible [7] to produce a Mott insulating state as might be anticipated; in fact the compound is metallic at least roughly as calculated. La438 consists of three layers of $LaNiO_2$ subject to quantum confinement, as we demonstrate below.

In La438 a simple ionic picture will give Ni configurations $d^8 + 2d^9$, which would suggest a natural identification of the one “inner” Ni1 $\equiv Ni^{2+}(d^8)$ and two outer Ni2 $\equiv Ni^{1+}(d^9)$ cations, as labeled in Fig. 1. Ni1-Ni2 layers are separated by only 3.25 Å, much less than the in-plane separation $a = 3.93$ Å, a characteristic that will become important below. The Ni trilayers are separated by the $La/O_2/La$ unit, and an ($a/2$, $a/2$, $c/2$) translation connecting successive NiO_2 trilayers reinforces very small interplanar coupling between cells, which will be shown to produce a natural quantum confinement within the trilayers.

Here we study the electronic structure of the compound by *ab initio* techniques to understand the electronic and magnetic structure of La438 and to identify the differences and similarities with respect to the cuprates. Our electronic

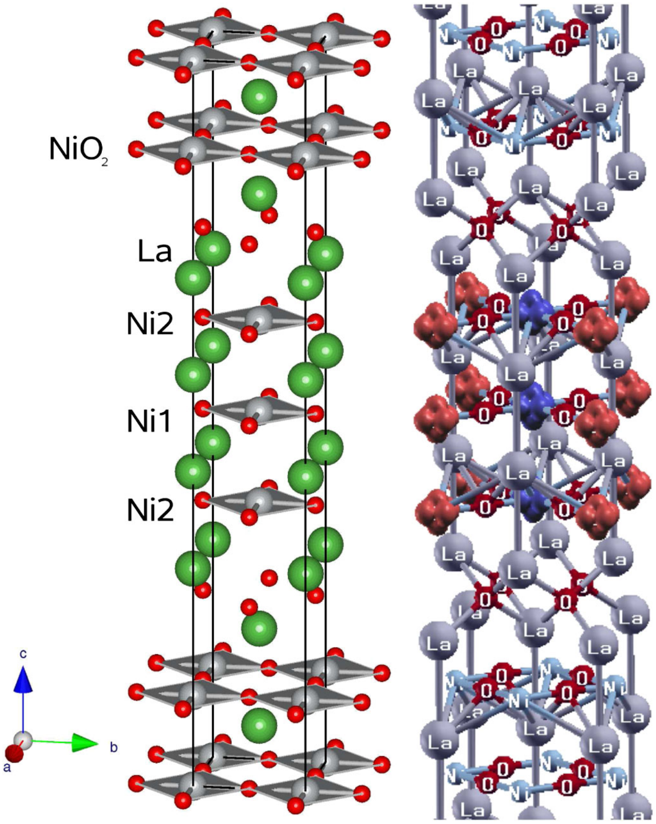

FIG. 1 (color online). Left side: structure of $La_4Ni_3O_8$, showing the three NiO_2 "infinite-layer" structures sandwiched on either side by the fluorite $La/O_2/La$ blocking layer. The Ni1 and Ni2 designations of the NiO_2 trilayer are provided. Right side: spin density isocontour plot of the ground state of $La_4Ni_3O_8$ from LDA + U calculations for the $\sqrt{2} \times \sqrt{2} \times 1$ cell. The different colors denote the two different spin directions. Magnetic order is AFM within layers, with spins aligned along the perpendicular (vertical) axis. Note that the two structures are rotated around the z axis with respect to each other.

structure calculations were performed within density functional theory [15] using the all-electron, full potential code WIEN2K [16] based on the augmented plane wave plus local orbital (APW + lo) basis set [17], and the experimental atomic positions [13]. The generalized gradient approximation [18] was used. To deal with strong correlation effects we apply the local density approximation (LDA) + U scheme [19,20] including an on-site repulsion U and Hund's coupling J for the Ni 3d states. Results were not very dependent on the specific values of U and J in the reasonable range, and we report results with $U = 4.75$ eV, $J = 0.68$ eV, values very similar to those determined from constrained density functional calculations [13].

The bands within LDA ($U = 0$) are metallic as expected, and in fact the bands crossing the Fermi energy E_F are dispersive (bandwidth of $\sim$2–3 eV). These bands do not suggest substantial effects of strong correlation, and Poltavets *et al.* suggested [13] Fermi surface driven spin density wave (SDW) order, which might destroy part of the Fermi surface and account for the magnetic transition. The earlier calculations, even those using LDA + U, produced only metallic states [13]. The key to obtaining a lower energy, and insulating, state is to allow extra freedom by doubling the lateral cell of La438, and we found that in-plane AFM order is readily obtained. Various configurations and types of spin order were tried, but no interplane AFM order could be obtained; moments along the z axis always want to align within the trilayer.

We discuss only this most energetically stable state, comprised of AFM-ordered Ni layers with spins aligned along the z axis. The spin density, pictured in Fig. 1, makes evident both the type of spin ordering and the character (shape) of the spin density, which reveals both $d_{x^2-y^2}$ and d_{z^2} contributions. There is indeed some charge difference with muffin-tin charges of 8.52 (Ni1) and 8.64 (Ni2), and somewhat differing moments of 1.4 and 1.3 μ_B respectively, accounted for by the hole occupation in the Ni 3d shells. It is understood that different formal charge states may involve surprisingly reduced difference in actual charge; it is magnetic states that are more instructive. While the moments we calculate might be consistent with an $S = 1$ configuration (d^8) reduced by hybridization, neither moment (1.3–1.4μ_B) can be ascribed to an $S = \frac{1}{2}\, d^9$ ion (which would have a maximum moment of 1 μ_B). Without spin-half d^9 ions, the ionic, charge-ordered picture becomes untenable, and a new mechanism for producing the gap must operate.

Our LDA + U band structure, shown in Fig. 2, produces a correlated (Mott) insulating state, but of an unusual type that requires broadening one's view of how these correlation effects operate. In the AFM state, the spin-up and spin-down band structures are of course identical. Since the valences of La^{3+} and O^{2-} are clear, the Ni ions are on average $Ni^{1.33+}$, with charge $d^{8.67}$ restricting the maximum moment to 1.33 μ_B, which is in fact what they are in our ground state. The Ni ions are fully polarized due to Hund's coupling, the result being that the majority orbitals are completely occupied and removed from consideration. Also, the minority $d_{x^2-y^2}$ orbitals are empty, centered at +3.5–4 eV on the energy scale of Fig. 2, each contributing one unit to the hole count, 1 μ_B to each Ni moment, and the in-plane superexchange coupling, but otherwise they are removed from the picture. The relevant orbitals are solely the partially occupied minority d_{z^2} orbitals on the six Ni ions in the AFM cell, which must accommodate one hole per triple (two in the AFM cell). The central question then is: how can a correlated insulating state, as we obtain, arise at "2/3 filling" if charge disproportionation into 2 Ni^{1+} + Ni^{2+} does not occur?

The in-plane AFM order, as is common, drastically reduces bandwidths (spin-conserving hopping takes place only between second Ni neighbors in the plane), so taking account of Ni d interlayer hopping $t_\perp$ (between Ni1 and Ni2) becomes important. For each Ni2-Ni1-Ni2 triple

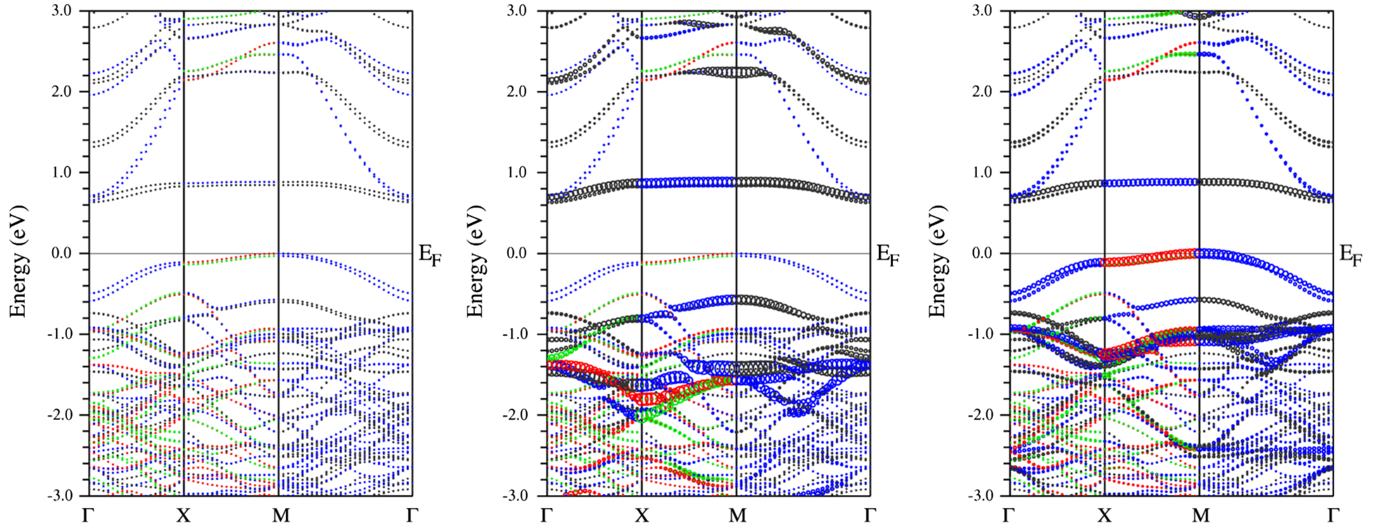

FIG. 2 (color online). The correlated insulating band structure of $La_4Ni_3O_8$ for the calculated ground state of Fig. 1. Left panel: the basic plot, allowing nearly degenerate bands to be distinguished. Other panels: $La_4Ni_3O_8$ fatband representation emphasizing (middle panel) Ni1, and (right panel) Ni2, d character. Note that the band at the bottom of the gap has vanishing Ni1 character.

along the z axis with neighbors coupled by $t_\perp$ (with zero site energy, neglecting the small on-site energy difference), the eigenvalues and eigenvectors are

$$E_j = 0, \quad \pm\sqrt{2}t_\perp, \quad |E_j> = \frac{1}{\sqrt{2}}(1, 0, -1), \quad \frac{1}{2}(1, \pm\sqrt{2}, 1). \tag{1}$$

The nonbonding (odd symmetry) state at $E_{j=0} = 0$ which does not involve the central Ni1 site is flanked below and above by even symmetry bonding (E_+) and antibonding (E_-) combinations. This coupling is pictured at the right of Fig. 3.

In the middle and right panels of Fig. 2 the Ni d characters are emphasized for Ni1 and Ni2, respectively. The bands display both the spectrum (most clearly evident near the M point) and the (Ni1 vs Ni2) character of this "triatomic molecule" entity. For example, the band at the bottom of the gap is (nonbonding) purely Ni2, which is E_0, while the other two bands have both Ni1 and Ni2 character (E_+, E_-). Two of these levels will be filled and one empty, separated by the gap. The size of the correlation-induced gap, which is 0.6 eV here, will depend both on the coupling $t_\perp$ and the value of U, rather than U alone.

Since previous LDA + U studies [12] produced only a metallic result, one can understand the electronic structure only by including intralayer AFM order and then using a

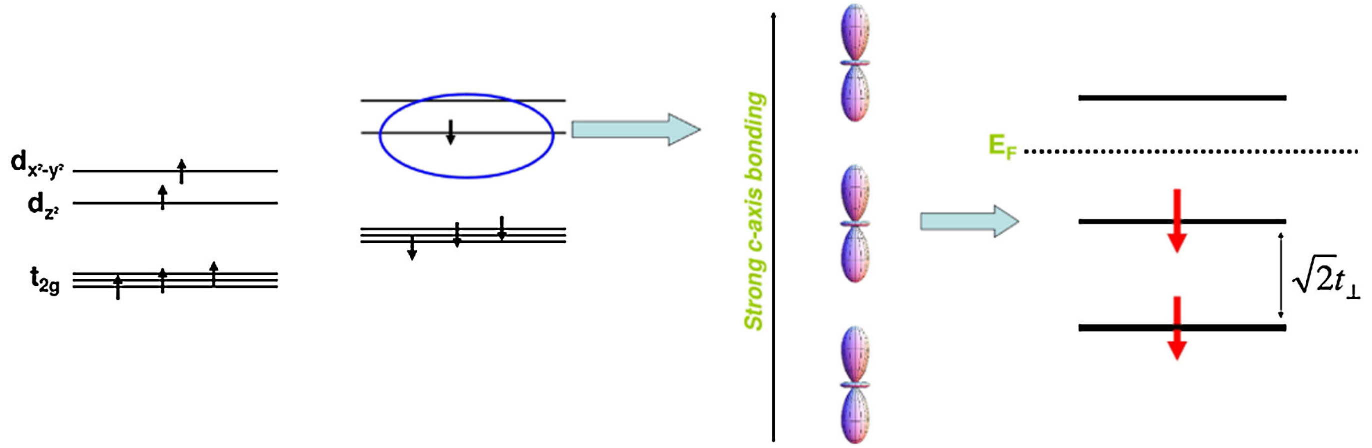

FIG. 3 (color online). Energy level diagram. The intra-atomic levels are shown on the left, with occupied majority states on the far left, partially occupied minority levels just to the right. The intra-atomic levels are crystal-field split according to the largely elongated octahedral environment. The right panel indicates how the minority-spin d_{z^2} orbitals on the Ni2-Ni1-Ni2 triple couple to give a gap at 2/3 band filling, following Eq. (1).

quantum-coupled unit, a *molecular trimer basis*, for the trilayer, from which on-site repulsion produces a correlated insulating state in agreement with observation [13]. The intralayer AFM magnetic coupling is strong and is mediated by $d_{x^2-y^2}$ superexchange, as in cuprates. Experimental data suggest an in-plane magnetic coupling with $J_{\parallel} \approx$ 120 K [13], which is substantial but an order of magnitude smaller than in cuprates. The Ni2-Ni1-Ni2 magnetic coupling across NiO_2 layers must be FM in sign to form the trimer orbitals. The coupling can also be viewed as double exchange, allowing the (confined, in this system) carriers to spread along $\hat{z}$ and form the molecular orbitals. This interpretation may help to explain the observed metallic behavior of $LaNiO_2$ (the $n \rightarrow \infty$ limit of the Ruddlesden-Popper sequence $La_{n+1}NinO_{2n+2}$), metallicity that is also obtained from the same type of calculations we have used here for $La_4Ni_3O_8$ [7]. We emphasize that this spin-aligned coupling along $\hat{z}$ is robust: we could not obtain antialigned layer magnetic order.

The trilayer-to-trilayer coupling along the c axis will proceed via superexchange through the fluorite $La/O_2/La$ spacer layer that can be seen in Fig. 1. The k_z bandwidth and related dispersion can be estimated from the splitting of the band below the gap near -0.5 eV at Γ (this splitting vanishes at π/c). The hopping $t_z \sim 15$ meV from a Ni2 ion to four Ni2 ions across the blocking layer leads to $J_z = 4t_z^2/U$ ~0.2 meV ~2 K. Such small interlayer coupling enters T_N logarithmically and can still give rise to magnetic order. However, the interslab coupling is frustrated as well as being small. These facts suggest that some of the entropy will not be lost at $T_N = 105$ K (full magnetic order along the z axis is not established), consistent with the small observed entropy change and also with the absence of a new diffraction peak [13] below T_N.

The state we have obtained and analyzed has insulating, AFM order in-plane in common with the HTS cuprates, as well as the obvious similarities in structure. The differences from cuprates are important to characterize, if the likelihood of promoting superconductivity is to be evaluated. First, excellent insulating character and relatively strong superexchange-mediated AFM order is obtained, but *without* integer formal oxidation states on the Ni ions. Such behavior has not been reported previously for transition metal oxides including cuprates, which have several three-Cu layer compounds that have ions with normal oxidation states. Second, the $d_{x^2-y^2}$ hole on each Ni ion is robust, and doped carriers go only into d_{z^2} states; hence the planar AFM order (driven by $d_{x^2-y^2}$ coupling) may be less affected and thereby survive to larger doping level than in cuprates. Orbital order, or coupled spin-orbital order, is ruled out as a participant in the insulating character. Another difference is that holes will enter the nonbonding band that is confined to the outer Ni2 layers with the Ni1 layer not participating in doping, whereas doped holes in cuprates go more or less into all layers equally. These doped holes may remain localized with the AFM Ni2 layers, delaying the insulator-to-metal transition to high doping levels. Doped electrons, on the other hand, will go into all three Ni layers but in a very specific way, with half of the charge on the central Ni1 layer.

The insulator-to-metal transition and loss of magnetic order may therefore occur in a very different manner than in the cuprates. Superconductivity coexisting with AFM order is one possibility, though the competition tends to be unfavorable for superconductivity. Doping of this system is likely to produce behavior quite different from that seen in existing layered transition metal oxides.

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