

Charge Disproportionation without Charge Transfer in the Rare-Earth-Element Nickelates as a Possible Mechanism for the Metal-Insulator Transition

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We study a model for the metal-insulator ($M-I$) transition in the rare-earth-element nickelates $RNiO_3$, based upon a negative charge transfer energy and coupling to a rocksaltlike lattice distortion of the NiO_6 octahedra. Using exact diagonalization and the Hartree-Fock approximation we demonstrate that electrons couple strongly to these distortions. For small distortions the system is metallic, with a ground state of predominantly d^8L character, where L denotes a ligand hole. For sufficiently large distortions ($\delta d_{Ni-O} \sim 0.05-0.10$ Å), however, a gap opens at the Fermi energy as the system enters a periodically distorted state alternating along the three crystallographic axes, with $(d^8\bar{L}^2)_{S=0}(d^8)_{S=1}$ character, where S is the total spin. Thus the $M-I$ transition may be viewed as being driven by an internal volume “collapse” where the NiO_6 octahedra with two ligand holes shrink around their central Ni, while the remaining octahedra expand accordingly, resulting in the $(1/2, 1/2, 1/2)$ superstructure observed in x-ray diffraction in the insulating phase. This insulating state is an example of charge ordering achieved without any actual movement of the charge.

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The perovskite rare-earth-element nickelates $RNiO_3$ undergo a first order metal-insulator ($M-I$) transition at a transition temperature T_{M-I} that can be tuned via pressure, strain, or variations in the radius of the R ion ($R \neq La$) [1,2]. These systems have received considerable attention for over two decades as a means for studying $M-I$ transitions; this has intensified in recent years due to proposals for application in heterostructures [3–5]. However, despite this long history, the precise mechanism for the $M-I$ transition is still not fully understood and a number of competing proposals have been made. These include a closing of the charge transfer gap [2], Jahn-Teller polarons [6], the formation of long-range magnetic order (if $R = Nd, Pr$) [7,8], charge ordering on the Ni sites, often referred to as charge disproportionation (CD) [1,9–15], or more complex charge ordering distributed over Ni and O sites as originally suggested by Mizokawa *et al.* [16] and recently followed up on [17–20] including the possible involvement of the lattice.

The leading interpretation for the $M-I$ transition is CD between the Ni sites. Several structural changes are concomitant with the $M-I$ transition, such as subtle changes in the Ni-O-Ni bond angle and changes in the Ni-O bond lengths resulting in a lowering of the crystal symmetry from an orthorhombic $Pbnm$ to a monoclinic $P2_1/n$ space group [1,9,12,13,21]. This forms two inequivalent Ni sites, where the NiO_6 octahedra contract and expand, respectively, about alternating sites along the three crystallographic axes. Formal valence counting suggests that the Ni^{3+} ions are in a $3d^7$ valence state and the inequivalent Ni sites are

interpreted as a $3d^7 3d^7 \rightarrow 3d^{(7-\delta)} 3d^{(7+\delta)}$ CD below T_{M-I} [9–11,14]. This CD is thought to drive the $M-I$ transition, however, it is not clear whether the electron-lattice or the on-site electron-electron interactions drive the charge ordering. T_{M-I} exhibits a large ^{16}O - ^{18}O isotope effect [6], confirming that the lattice and electronic degrees of freedom are strongly coupled, and the latter could be driven by the former. This is supported by a recent pump-probe experiment, where large changes in resistivity of $NdNiO_3$ thin films were driven by excitation of phonon modes of the substrate which couple to either the bond-stretching or rotational modes of the film [20]. A recent proposal views the lattice distortion as a secondary effect to a magnetic ordering [7,8], however, this picture is difficult to apply to systems with $T_N < T_{M-I}$, which is the case across much of the phase diagram [1].

The CD scenario assumes that Ni $3d^7$ is the appropriate starting point for describing the nickelates, but a few open issues remain. In the (nearly) cubic structure, the Ni $3d^7$ ($t_{2g}^6 e_g^1$) ion has two degenerate e_g orbitals which the system will prefer to lift via a coherent Jahn-Teller (JT) effect or via CD between neighboring Ni sites. There is no sign of a JT distortion [6] like the orbital ordering in manganites [22], which also have a singly occupied degenerate e_g orbital. On the other hand, CD should be suppressed by the large Hubbard U , however, it can be stabilized by a sizable Hund's coupling if the system is close to the itinerant limit [23]. This is likely the case in the rare-earth-element nickelates, which have been classified as small or negative charge transfer systems [16–18,24–30]. Under such

conditions it becomes energetically favorable to transfer a hole from Ni to ligand O sites [31], and Ni $3d^7$ is no longer the appropriate starting point. Rather, one should begin with a Ni $d^8\bar{L}$ state in the atomic limit, which is equivalent to taking a negative charge transfer energy Δ before allowing for hybridization between the Ni and O atoms. In this picture, the ground state would have, on average, one ligand hole per NiO_3 unit.

Ligand holes can couple strongly to the bond-stretching O vibrations which modulate the hybridization between the transition metal and O sites [6,32]. Thus, the carriers in nickelates (which are primarily O ligand holes in this picture) can couple strongly to the rocksaltlike lattice distortions. In this Letter, we examine this scenario as a means for explaining the $M-I$ transition. Using exact diagonalization (ED) and Hartree-Fock (HF) calculations [33,34] we confirm that a strong electron-lattice coupling drives the system through a $M-I$ transition for sufficiently large and experimentally relevant lattice distortions ($\delta d_{\text{Ni-O}} \sim 0.05\text{--}0.1 \text{ \AA}$). In the insulating phase we find a novel charge ordering which can be viewed as a $(d^8\bar{L})_i(d^8\bar{L})_j \rightarrow (d^8\bar{L}^2)_{S=0}(d^8)_{S=1}$ type, where S is the total spin. In this picture, the $M-I$ transition results from a partial volume collapse of NiO_6 octahedra with two ligand holes around their central Ni, while the other octahedra expand accordingly with little net effect on the total volume, as observed experimentally [1]. However, since each O is shared by a collapsed and an expanded octahedron, in fact all octahedra have the same average hole concentration. The difference is that the two ligand holes acquire the symmetry of the e_g orbitals of the Ni in the collapsed $d^8\bar{L}^2$ octahedron, which therefore becomes formally equivalent to a $3d^6$ state that is effectively no longer JT active, and attains a spin of zero. Thus, as far as symmetry and spin are concerned, this state appears as a fully CD state, but one achieved without actual movement of charge. We note that the present study using ED methods and HF theory complements recently published studies in support of Mizokawa *et al.* [16] suggestion using dynamical mean-field theory + density functional theory (DFT) [17] and DFT [19] methods.

We investigate quasi-one-dimensional (1D) and three-dimensional (3D) clusters or unit cells. In each case, the orbital basis includes both $3de_g$ orbitals at each Ni site and the $2p_\sigma$ orbital at each O site, as shown in Fig. 1. The microscopic Hamiltonian for the electronic degrees of freedom is $H = H_0 + H_{\text{int}}$, where

$$H_0 = \sum_{i,\alpha} \epsilon_\alpha d_{i,\alpha,\sigma}^\dagger d_{i,\alpha,\sigma} + \sum_{i,j,\alpha,\beta,\sigma} t_{ij}^{\alpha\beta} d_{i,\alpha,\sigma}^\dagger d_{j,\beta,\sigma}$$

contains the noninteracting on-site and near-neighbor hopping terms, and

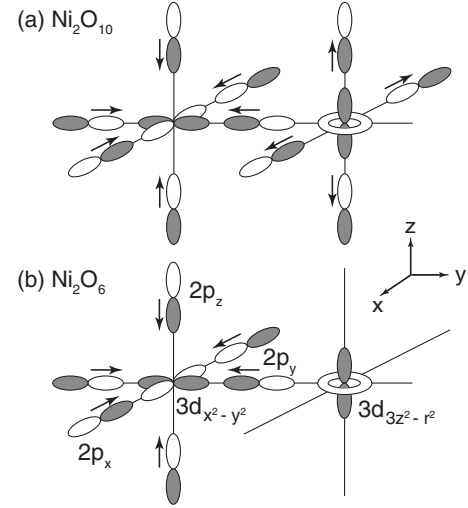


FIG. 1. (a) Ni_2O_{10} quasi-1D cluster with periodic boundary conditions along the y axis, studied with ED. Both Ni $3d e_g$ orbitals are included at each Ni site, but only one orbital per Ni is depicted here to establish our phase convention. (b) Ni_2O_6 unit cell used for our 3D calculations using HFA. The arrows in both panels indicate the displacement pattern for the rocksaltlike oxygen distortion.

$$H_{\text{int}} = \sum_{i,\alpha,\sigma \neq \sigma'} \frac{U}{2} n_{i,\alpha,\sigma} n_{i,\alpha,\sigma'} + \sum_{i,\alpha \neq \alpha',\sigma,\sigma'} \frac{U'}{2} n_{i,\alpha,\sigma} n_{i,\alpha',\sigma'} + \sum_{i,\alpha,\alpha',\sigma,\sigma'} \frac{J}{2} d_{i,\alpha,\sigma}^\dagger d_{i,\alpha',\sigma'}^\dagger d_{i,\alpha,\sigma} d_{i,\alpha',\sigma'} + \sum_{i,\alpha \neq \alpha',\sigma \neq \sigma'} \frac{J'}{2} d_{i,\alpha,\sigma}^\dagger d_{i,\alpha',\sigma'}^\dagger d_{i,\alpha',\sigma'} d_{i,\alpha,\sigma}$$

contains the on-site Coulomb interactions with $n_{i,\alpha,\sigma} = d_{i,\alpha,\sigma}^\dagger d_{i,\alpha,\sigma}$, where $d_{i,\alpha,\sigma}^\dagger$ creates a spin- σ electron in one of the two e_g orbitals if i is a Ni site, or the $2p_\sigma$ orbital if i is an O site. In eV units we set $U_d = 7$, $J_d = J'_d = 0.9$, $U'_d = U_d - 2J_d$, $U_p = 5$, $\epsilon_d = 0$, $\epsilon_p = 2.25$, $(pd\sigma) = -1.8$, $(pp\sigma) = 0.6$, $(pd\pi) = -(pd\sigma)/2$, and $(pp\pi) = -(pp\sigma)/4$. For these parameters the ground state of an isolated NiO_6 octahedron is $|\Psi\rangle = \alpha|d^7\rangle + \beta|d^8\bar{L}\rangle + \gamma|d^9\bar{L}^2\rangle$ with $\beta^2 \approx 0.56$, i.e., the system is in the negative charge transfer regime and the ground state has predominantly $d^8\bar{L}$ character, in agreement with experiment [24–27].

The lattice degrees of freedom are treated in the adiabatic limit as frozen lattice displacements [35], i.e., all O atoms are displaced equally along the rocksalt displacement pattern indicated by arrows in Fig. 1. The electron-lattice coupling is introduced by rescaling the Ni-O and O-O transfer integrals. Specifically, we take $t_{pd} = t_{pd}^0(1 + \delta d_{\text{Ni-O}}/d_{\text{Ni-O}})^{-3}$ and $t_{pp} = t_{pp}^0(1 + \delta d_{\text{O-O}}/d_{\text{O-O}})^{-4}$ [18,36], where δd is the change in the appropriate bond length with respect to $d_{\text{Ni-O}} = d_{\text{O-O}}/\sqrt{2} = 1.95 \text{ \AA}$ in the undistorted structure. The lattice potential energy adds an overall quadratic term to the total energy, while the lattice kinetic energy is neglected. From now on all displacements

are reported in terms of $\delta d_{\text{Ni-O}}$, and we drop its subscript for brevity. We have also tested the other possible displacement patterns for the O atoms. The pattern discussed here produces the lowest energy [37]. Finally, we note that the cluster and unit cell considered here are too small to capture the lower-temperature magnetic transition, which is beyond the scope of our work.

We first consider two neighboring NiO_6 octahedra in the quasi-1D cluster of Fig. 1(a) with three holes per Ni; this can be solved exactly using ED. Fig. 2(a) shows the electronic contribution to its ground state energy E_{el} in the $(3\uparrow 3\downarrow)$ and $(4\uparrow 2\downarrow)$ sectors as a function of δd . Figures 2(b) and 2(c) show average hole occupations at Ni and O sites for the compressed (solid symbols) and expanded (open symbols) NiO_6 octahedra. Both sectors exhibit a sizable decrease in the electronic energy with increasing displacement, indicating a rather strong electron-lattice coupling. The $(3\uparrow 3\downarrow)$ sector exhibits a kink in E_{el} for a critical displacement $\delta d_c \sim 0.097 \text{ \AA}$, indicative of a level crossing and a change in the ground state wave function as a function of displacement.

For $\delta d = 0$ the ground state has a total spin $S_{\text{tot}} = 0$ with majority $(d^8 \underline{L})(d^8 \underline{L})$ character, as expected for a negative value of Δ . This state persists as the ground state for small $\delta d < \delta d_c$, however, a small redistribution of charge occurs between the two octahedra due to the increased delocalization on the compressed side. For $\delta d > \delta d_c$ a different ground state is obtained with $S_{\text{tot}} = 1$ and $m_z = 0$. (In the $4\uparrow 2\downarrow$ sector the $S_{\text{tot}} = 1$, $m_z = \pm 1$ counterparts of this

state form the degenerate ground state for all values of δd .) The new state possesses an interesting redistribution of charge. Both Ni ions are in a d^8 spin triplet state while the \underline{L} hole of the expanded octahedron transfers to the compressed side, where the two \underline{L}^2 holes lock in a triplet pair due to the finite value of U_p [38]. The \underline{L}^2 spin couples antiferromagnetically to the central Ni spin, leaving the system in a $(d^8 \underline{L}^2)_{S=0}(d^8)_{S=1}$ state. Thus, for sufficiently large rocksaltlike displacements, the ligand hole of the expanded octahedron can reassociate with a neighboring NiO_6 octahedron leaving a lone $S = 1$ spin on alternating Ni sites and a small CD ~ 0.1 between the two inequivalent Ni sites. We note that the critical value δd_c obtained here is slightly larger than the typical changes in bond length $\sim 0.052\text{--}0.092 \text{ \AA}$ reported in the insulating phase [9,10,14].

Below the M - I transition a rocksalt distortion exists in the nickelates and a similar reassociation of the ligand holes may occur in the 3D system as well. However, while for the Ni_2O_{10} cluster we can assign the O sites to unique octahedra, in the bulk 3D system this is not possible since each O is shared by an expanded and a contracted octahedron. The \underline{L}^2 triplet pairs assigned with the collapsed NiO_6 octahedra are formed between the ligand hole of the compressed NiO_3 unit and a second hole provided by the neighboring expanded NiO_3 units. From a charge counting perspective, each of the NiO_3 units still has one ligand hole and hence the system appears to have dominant $d^8 \underline{L}$ character. What is changed is not the ligand holes' average distribution, but the phases in their wave function which now acquire the symmetry of the two e_g orbitals of the Ni in the collapsed octahedron. The basic effect is similar to the Zhang-Rice singlet scenario in the cuprates where the ligand hole selects the relative phases of the four oxygen orbitals so as to maximally hybridize with one of the two Cu ions bridged by the oxygen [39].

We stress that this is a very different form of charge ordering than the commonly discussed CD; it should be thought of as a novel charge ordering without a significant movement of charge.

We now turn to a quantitative analysis of the 3D case, and examine an extended lattice that cannot be handled using ED. We therefore implement an unbiased Hartree-Fock approximation (HFA) [34] (see the Supplemental Material for details [37]). One might doubt the validity of the HFA given the strong correlations on the Ni sites, however, the large bandwidth O $2p$ bands overlap with the Ni states because of the negative charge transfer energy. This reduces significantly the effects of correlations, explaining why a number of studies have had success with mean-field approaches [16,18,24]. To verify that the HFA captures the physics of our model we compare its predictions to ED results for a Ni_2O_6 cluster with periodic boundary conditions, see Fig. 1(b). E_{el} results are shown in Fig. 3(a). Not surprisingly, the HFA has higher ground state energies ($\sim 1 \text{ eV}$), but it correctly reproduces the

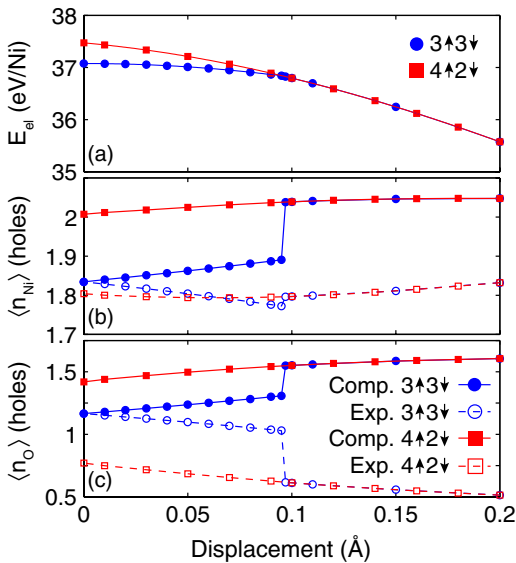


FIG. 2 (color online). A summary of ED results for the Ni_2O_{10} cluster. (a) Electronic contribution to the ground state energy in the $(3\uparrow 3\downarrow)$ (blue circle) and $(4\uparrow 2\downarrow)$ (red square) sectors as a function of the static O displacement. (b),(c) Average hole occupancy at Ni and O sites, respectively. Sites on the left (right) side of the Ni_2O_{10} cluster correspond to the compressed (expanded) NiO_6 octahedron for $\delta d > 0$ (see Fig. 1), and are represented by the solid (open) symbols.

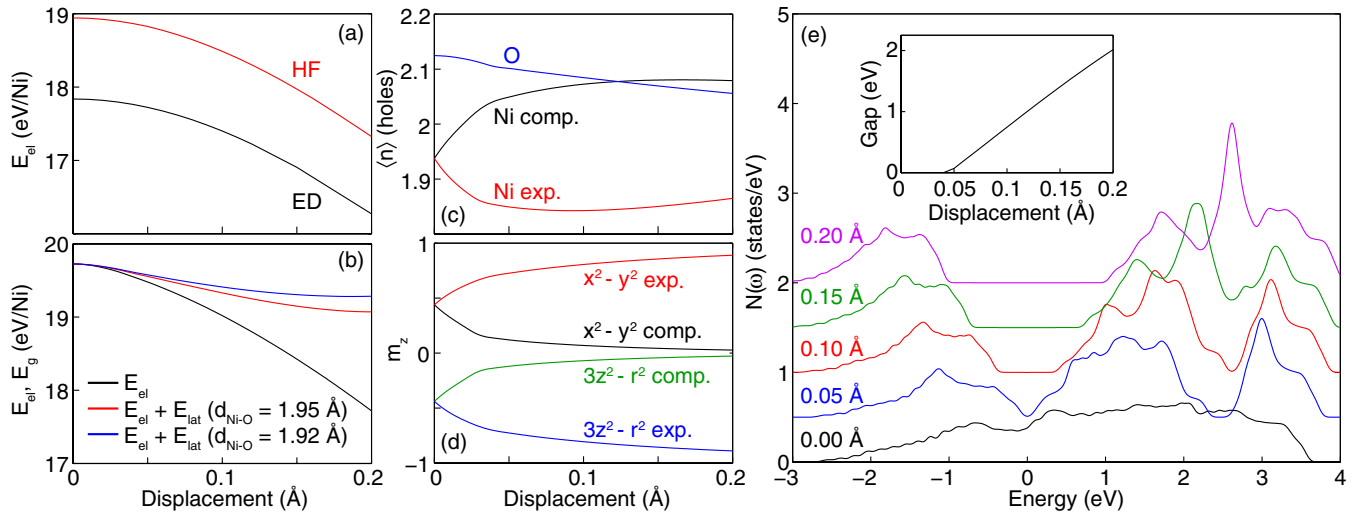


FIG. 3 (color online). (a) A comparison of the HFA [red (light)] and ED [black (dark)] ground state energies as a function of the oxygen displacement for the Ni_2O_6 cluster, containing only $\mathbf{k} = 0$. (b)–(e) HFA results for the 3D lattice with $80^3/2$ \mathbf{k} points in the Brillouin zone: (b) Ground state electronic energy, (c) Average hole occupation of the oxygen (blue) sites and the compressed (black) and expanded (red) Ni sites. Note that the lattice distortion retains the local cubic symmetry about each Ni site so no orbital polarization of the Ni e_g orbitals occurs. (d) Magnetization $m_z = (n_\uparrow - n_\downarrow)$ of the Ni orbitals. (e) single particle density of states for several oxygen displacements. The spectrum has been lifetime broadened with a Lorentzian (half width at half maximum = 25 meV). The inset shows the gap as a function of displacement.

displacement dependence and the average hole occupations [37]. This gives us confidence that HFA is reasonably accurate for this Hamiltonian.

Scaling to the extended lattice, Figs. 3(b)–3(e) show HF results obtained for a 3D system with 0.5×80^3 momentum points in the Brillouin zone. The electronic component of the ground state energy E_{el} [Fig. 3(b)] essentially mirrors the ED results, exhibiting large variation with lattice displacement. This confirms the strong electron-lattice coupling even within the HFA. The hole occupancies n [Fig. 3(c)] and Ni magnetization m_z [Fig. 3(d)] also follow the expectations gained from the Ni_2O_{10} cluster. For small δd the total occupancies of the two Ni sites start to separate until $\delta d \sim 0.03$ to ~ 0.04 Å, when they gradually level off. At the same time the magnetizations of the two e_g orbitals in the compressed octahedron fall to zero as each e_g orbital is occupied by half an electron of each spin species, on average. Similarly, the magnetization of each e_g orbital in the expanded octahedron rapidly grows to nearly one but with opposite alignments. The magnetization of the O sites (not shown) is nearly zero for all values of δd . Although the HFA cannot reproduce the triplet correlations of the exact cluster solution, these results mimic the $(d^8 \underline{L}^2)_{S=0} (d^8)_{S=1}$ ground state observed in the small cluster and therefore confirm this valence electron redistribution between O and Ni.

Next, we calculate the single particle density of states $N(\omega)$ as a function of δd , see Fig. 3(e). For $\delta d = 0$, $N(\omega)$ has finite weight at the Fermi energy $\omega = 0$, consistent with metallic behavior in a negative charge transfer system. $N(\omega = 0)$ is suppressed for increasing δd until $\delta d \approx 0.05$ Å, where a gap that increases linearly with δd

opens up [inset, Fig. 3(e)]. We stress that this gap is the result of the alternating expanded and contracted octahedra rather than the formation of the $(S = 0)_i (S = 1)_j$ magnetic structure, because similar sized gaps are observed even when we restrict the HFA by enforcing identical Ni sites. We conclude that the gap opens due to the electron-lattice interaction and rocksalt lattice distortions, consistent with the $M-I$ transition observed in these materials.

We complete our discussion with an estimate for the energy cost of the octahedral distortions, based on DFT within the generalized gradient approximation [40,41]. The total energy was calculated for the cubic $LaNiO_3$ structure with lattice constants of 3.9 and 3.84 Å, the latter being the DFT prediction [37]. In both cases we find the change in total energy to increase like $(\delta d)^2$. We use this change in total energy as a very rough estimate of the potential energy of the lattice distortion [42]. Figure 3(b) shows the total energy obtained by adding this contribution to E_{el} obtained from the HFA. The total energy possesses a deep minimum for $\delta d \sim 0.17$ – 0.2 Å. This is a factor of 2 larger than the experimental value, but reasonable given the crudeness of our estimate. A strong isotope effect is obviously consistent with this model of the $M-I$ transition.

In summary, we have examined the consequences of the interplay between a negative charge transfer energy and the electron-lattice coupling in $RNiO_3$, starting from a $d^8 \underline{L}$ atomic configuration. Our results provide detailed insight into the physics of the $M-I$ transition, involving strong correlations, O $2p$ holes providing metallic charge carriers, and strong electron-lattice coupling providing distortions resulting in an insulating state. In this picture, the

nickelates undergo an effective CD achieved without any significant movement of charge between neighboring NiO₆ octahedra. In order to verify whether such a picture extends across the whole family of nickelates, systematic studies capable of incorporating more accurately the lattice potential are required.

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