

Charge Ordering as Alternative to Jahn-Teller Distortion

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We show that the Mott transition in orbitally degenerate systems can, and often does, proceed not in the standard “Mott insulator—weakly correlated metal” sequence, but via a novel intermediate phase with a charge (rather than orbital) ordering. Lifting an orbital degeneracy this way can be viewed as an alternative to a Jahn-Teller distortion. This may occur in a crossover between localized and itinerant regimes, if Hund’s rule coupling overcomes the on site Coulomb repulsion. We show both by calculations and by experiment that this scenario is realized in rare-earth nickelates, and argue that the same phenomenon takes place in many other systems.

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A partially occupied degenerate level is usually unstable against a distortion that splits the level and lowers the occupied states, the Jahn-Teller (JT) effect. One can say, paraphrasing Aristotle, that Nature abhors an orbital degeneracy. In solids this takes form of a cooperative JT effect [orbital ordering, (OO)], when the lattice distorts coherently so as to lift the orbital degeneracy at each site. This requires narrow bands, and is unavoidable in localized Mott-Hubbard systems with an orbital degeneracy. Upon a gradual delocalization of degenerate electrons, the JT distortion and corresponding OO become less favorable, and in itinerant metals orbital degeneracy does not lead to OO.

Typical JT distortions create a crystal field of the order of 0.1–0.5 eV, and a band much wider than that will not be subject to a JT instability: for broad bands the kinetic energy dominates and suppresses the JT transition. Thus, the presence (absence) of a JT distortion is often used as an empirical litmus test for localized (itinerant) electronic states. As often in physics, nontrivial effects appear in the crossover regime. If one gradually moves from a localized Mott insulator to an itinerant metal, at some point the Coulomb scale U becomes comparable with the kinetic energy scale W (bandwidth), and with the intraatomic (Hund) magnetic scale J_H . As we show below, a realistic J_H may overcome the on site repulsion and create a new intermediate phase instead of a conventional Mott transition, wherein the orbital degeneracy is lifted via charge ordering (CO) (also known as charge disproportionation or charge density wave), so that, e.g., at half of all sites a degenerate level becomes empty, and at the others doubly occupied. This way, the system *gets rid of orbital degeneracy by getting rid of a degenerate electron*. We demonstrate that this effect takes place in rare-earth nickelates, especially with small ions (YNiO₃, LuNiO₃). Apparently the same mechanism operates in some layered nickelates,

in perovskite and layered ferrates, and in many other similar materials.

We want to compare two states: one with one electron on a doubly degenerate level and with eventual JT distortion, and the other with CO, that is, with nondegenerate d^0 and d^2 configurations at two sites. To be specific, we consider the Ni³⁺ ion in an e_g^1 state that can disproportionate into a Ni²⁺ (e_g^2) and a Ni⁴⁺ (e_g^0) state. The relevant energies can be estimated from a degenerate Hubbard model:

$$H = \sum_{i \neq j, \alpha\beta} t_{i\alpha j\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + U \sum_{i, \alpha\sigma \neq \beta\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} - J_H \sum_{i, \alpha \neq \beta} \vec{S}_{i\alpha} \vec{S}_{i\beta} - \sum \{E_{JT} + E_{\text{breath}}\}. \quad (1)$$

Here J_H is the Hund rule interaction, E_{JT} is the energy gain due to a JT distortion for Ni³⁺, E_{breath} is the energy regained by allowing oxygens to breath around Ni⁴⁺ and Ni²⁺ in case of CO, and i , α , and σ are site, orbital, and spin indices, respectively. The local levels and their occupations in this simple model are shown in Fig. 1(a) (JT) for the 2Ni³⁺ and in Fig. 1(b) (CO) for the Ni²⁺ + Ni⁴⁺ configurations, where the respective energies are shown. For the CO state there is an energy loss of U and an energy gain of J_H . Although usually $J_H \sim 1$ eV $\gg E_{JT}$, in the localized limit $U \gg J_H$, and the JT state is the ground state, even though the effect of U is mitigated by the screening due to O breathing (E_{breath}). However, with delocalization of the e_g electrons (i.e., broadening the levels in Fig. 1 into bands), the occupation of the d_{z^2} and $d_{x^2-y^2}$ levels (now bands) is not 1 and 0 any more, but rather ν and $1 - \nu$, with $\nu \rightarrow 0.5$ as the bandwidth becomes much larger than the JT splitting. The energy gain E_{JT} is then reduced from $2E_{JT}$ to $2|2\nu - 1|E_{JT}$. In such a case, the Hubbard description of the Coulomb interaction is becoming increasingly less adequate with delocalization,

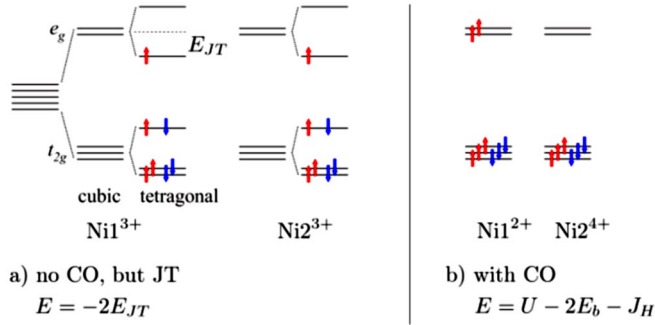


FIG. 1 (color online). Schematic electronic level diagram of Ni ions in $RNiO_3$ in two cases: (a) two JT distorted Ni^{3+} ions (energy gain E_{JT} per site), and (b) charge disproportionation.

and in the fully delocalized limit, the additional Coulomb energy due to CO is reduced to the Hartree energy, a very strong reduction. Furthermore, delocalization often leads to metallization, and thus to screening that further diminishes the effect of the Coulomb repulsion. This reduction of the effective U is especially strong in systems with a small or negative charge-transfer gap and large contribution of oxygen holes, to which nickelates belong.

Unlike U , the Hund rule coupling J_H is hardly sensitive to delocalization, so that the energy gain associated with CO is much more robust against band formation. It is also less sensitive to the value of the charge transfer: in the itinerant band picture even an incomplete charge transfer $\delta n < 1$ can (and often does) correspond to complete or nearly complete spin polarization with $S = 1$ on one site and $S = 0$ on the other (a band may be fully polarized yet be composed of a mixture of the Ni1 and Ni2 states). Thus, there may be a crossover region where the CO schematized in Fig. 1(b) is stable with respect to both the high-symmetry phase and the JT state. We will show that this happens in perovskite nickelates $RNiO_3$, especially with small rare earths $R = Lu, Y$, where low-spin Ni^{3+} ions are JT ions with the original configuration $t_{2g}^6 e_g^1$. We will also identify some other systems where similar effects take place.

Perovskite nickelates with small rare earths exhibit a metal-insulator transition at a temperature $T_{MI} = 640\text{--}670$ K. Simultaneously the symmetry lowers from orthorhombic to monoclinic, with two inequivalent Ni ions [1], Ni^{2+} ($t_{2g}^6 e_g^2$) and Ni^{4+} ($t_{2g}^6 e_g^0$) (although the actual charge disproportionation is much less than one, we can still use the integer valence values, keeping in mind that they are quantum numbers of the respective states rather than actual charges). At lower temperatures these systems develop a nontrivial $\uparrow\downarrow\downarrow$ antiferromagnetic order [2,3]. With the increase of the ionic radius of R the Ni-O-Ni bond angle increases, the bands widen, and T_{MI} goes down. In $NdNiO_3$ and $PrNiO_3$ the insulator-metal and magnetic transitions occur simultaneously as a first order transition; but below T_c the same, although weaker, charge segregation occurs, with a transition to a monoclinic phase [4]. And, finally, in $LaNiO_3$ the bands become so broad that

even the magnetic instability disappears and it remains a paramagnetic metal down to the lowest temperatures.

The insulator-metal transition and the unusual magnetic structure in $RNiO_3$ are apparently connected to the charge disproportionation. Experimentally, the charge ordering manifests itself in oxygen breathing and in different magnetic moments on the two Ni sites, e.g., $1.4\mu_B$ for Ni^{4+} and $0.7\mu_B$ for Ni^{2+} in $YNiO_3$ and $LuNiO_3$ [3], respectively, or $1.4\mu_B$ and $0.6\mu_B$ for $HoNiO_3$ [5].

A close inspection of these compounds shows that, contrary to popular believe, they cannot be described as Mott-Hubbard insulators. It appears that a more conventional band picture gives a better description. In particular, it is capable of explaining the charge segregation that occurs in the crossover region between localized and itinerant states along the lines outlined above. Indeed, our band structure calculations [6], Fig. 2, show that optimization of the nonmagnetic (not allowing magnetic moments on Ni) crystal structure (relaxing the O positions keeping the cell dimensions fixed) leads to hardly any difference between Ni1 and Ni2; at the same time, the O octahedra become substantially ($>5\%$) JT distorted. The magnetic solutions (either ferromagnetic or antiferromagnetic), with the exchange splitting fully operating, lead to strong inequivalence of these Ni's: Ni1 has practically the configuration $t_{2g}^6 e_g^2$, and Ni2 $t_{2g}^6 e_g^0$, corresponding, respectively, to Ni^{2+} and Ni^{4+} . The calculated moments are 1.25 and $0.28\mu_B$, in reasonable agreement with the experiment. The resulting ratio of the bond valence sums $\sum d_{Ni^{2+}-O}^2 / \sum d_{Ni^{4+}-O}^2 = 1.025$ is close to the experimental value of 1.037. These results clearly show that the proposed mechanism of charge ordering relies heavily on the energy gain due to an exchange splitting (Hund's rule energy gain), which is actually a local property and does not strongly depend on the detailed type of magnetic ordering (or on the presence of a magnetic long-range order at all). On the other hand, it requires that the starting state have an orbital degeneracy, as opposed to other known cases of charge disproportionation, such as $2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$ or $2Pb^{3+} \rightarrow Pb^{2+} + Pb^{4+}$, where the instability is due to the atomic tendency to have either fully empty or fully occupied shells.

According to the presented scenario, $RNiO_3$ compounds may be treated as band insulators with a gap forming between the spin-up e_g band of Ni^{2+} and the (hardly spin-polarized) e_g band of Ni^{4+} [see Fig. 2 (bottom)], as opposed to earlier interpretations in terms of a Mott-Hubbard gap [7], a Ni-O charge-transfer gap [8], or an inhomogeneous phase [9]. Since local density approximation (LDA) calculations usually underestimate the value of the energy gap but correctly reproduce the trend in its pressure dependence, we decided to check the resulting picture experimentally by studying the behavior of $RNiO_3$ under pressure.

A Mott (or charge-transfer) insulator and a band insulator behave differently under pressure. The former usually

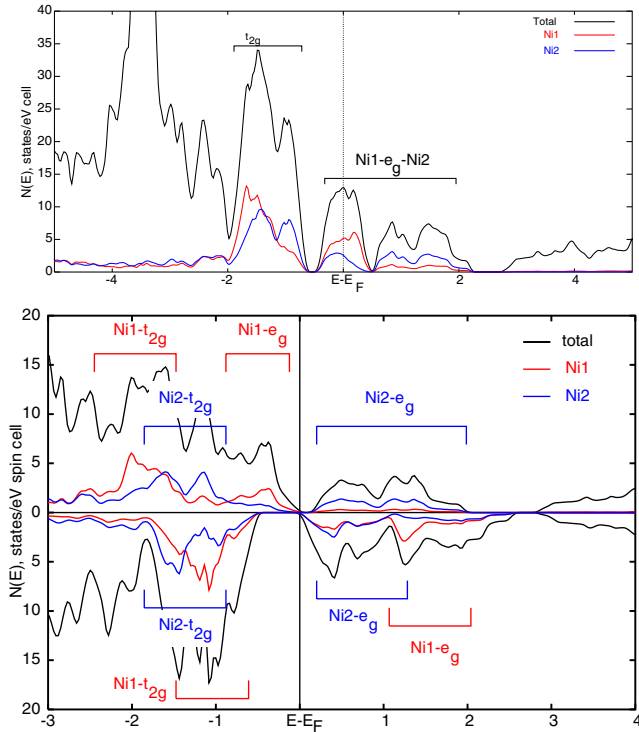


FIG. 2 (color online). Densities of states (DOS) for the hypothetical nonmagnetic (top) and ferromagnetic (bottom) LuNiO_3 in the experimental low-temperature structure [1]. The brackets roughly indicate the energy span of the bands with a particular character. Note that the magnetic e_g bands, despite strong hybridization, clearly split into two sets, one predominantly derived from the Ni^{2+} states and another from the Ni^{4+} ones, the latter being about 1 eV higher due to the shorter Ni-O bonds and thus stronger p - d hybridization for Ni^{4+} . The antiferromagnetic DOS is practically the sum of the two components of the ferromagnetic DOS.

undergoes a first order transition at a rather high pressure, when the band widths surpass U , with a jump in resistivity and a big gap in the insulating phase (defined by the large U). On the other hand, an intermediate phase between strongly localized and itinerant regime, such as the CO phase described above, may be better described as a band insulator. In this case under pressure one should observe a semiconducting behavior with the gap smoothly going to zero and disappearing at the transition, which requires an increase of the band widths of the order of the zero-pressure gap that is much smaller than the Hubbard U . At the critical pressure the gap at $T = 0$ is exactly zero, and one expects the effective number of carrier to grow with temperature as a power of T . Combined with the T dependence of the scattering rate, this can produce resistivity that is metallic at low T and semiconducting at high T , typical for systems with pseudogaps. Furthermore, we expect for our mechanism that the CO disappears at a higher pressure than that for the metal-insulator transition: in the band picture, an energy gain will be present as long as the centers of gravity of the corresponding bands are well separated in energy.

To test this, we have studied the effect of pressure on the transport, magnetic, and structural properties of LuNiO_3 with $T_{\text{MI}} \approx 599$ K [1] and $T_N \approx 130$ K [10]. The samples were synthesized under pressure in CSIC, Madrid. Measurements of the electrical resistance up to 23 GPa between 4.2 and 300 K were performed in a diamond anvil cell using the standard four-probe dc method. Magnetization was measured using a Quantum Design magnetometer. High pressure neutron powder diffraction data were collected on the PEARL beam line at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. The results are summarized in Fig. 3. With increasing pressure the semiconducting behavior gradually changes to metalliclike, indicating a pressure-induced metal-insulator transition already at about 6 GPa. The kink in $R(T)$ curves at T_{max} is due to the onset of antiferromagnetism at T_N and shifts at low pressures to higher temperatures with pressure; see Fig. 3(b). This is confirmed by magnetization measurements up to 1.5 GPa which reveals an increase of T_N with pressure as $d \ln T_N / dP = 3.3 \times 10^{-2} \text{ GPa}^{-1}$, very close to the values obtained for $R\text{NiO}_3$ compounds with $R = \text{Eu, Sm, Gd}$ [11]. Although we do not have an independent proof of magnetic ordering at higher pressures, the assumption that T_{max} is related to T_N would imply the existence of antiferromagnetism in the metallic state. Such a pressure-induced magnetic metallic state has been recently observed in EuNiO_3 [12]. On the other hand, from high

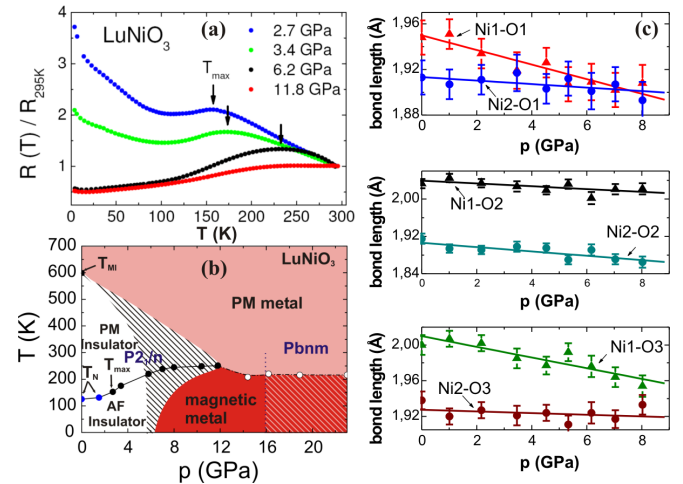


FIG. 3 (color online). (a) Temperature dependence of the LuNiO_3 resistance at selected pressures. (b) Proposed phase diagram for LuNiO_3 . T_N is the Neél temperature as determined from high pressure magnetization measurements. T_{max} is deduced from the temperature dependence of the resistivity $R(T, P)$ as a function of pressure: in the low pressure region, $0 < P \leq 11.8$ GPa, from $\partial R / \partial T = 0$ (●), and above 11.8 GPa from the minimum of $\partial^2 R / \partial T^2$ (○). The crossover region between the insulating and metallic state is hatched. The metallic and possibly magnetic monoclinic phase is marked by the dark (red) area. The vertical dashed line at $P = 16$ GPa indicates the monoclinic ($P2_1/n$) to orthorhombic ($Pbnm$) phase transition [15]. (c) Pressure dependence of the Ni-O bond lengths in LuNiO_3 .

resolution neutron diffraction measurements we find that in LuNiO₃ the magnitude of the breathing distortion remains nearly constant up to 8 GPa (the highest pressure at which neutron scattering measurements were done). The ratio of the NiO₆ octahedra volumes are 1.118 at $P = 0$ and 1.116 at $P = 8$ GPa. However, the Ni-O bond lengths of the two Ni sites along the c axis (Ni1-O1 and Ni2-O1, respectively) become nearly equal at $P = 8$ GPa. This indicates the beginning of a gradual anisotropic melting of the CO with pressure (already in the metallic phase), inequivalence of Ni1 and Ni2 surviving up to a higher $P \sim 16$ GPa, where monoclinic-orthorhombic transition takes place; see Fig. 3(b).

Another indication that these materials cannot be described as Mott insulator comes from our LDA + U calculations. Using the experimental structure at $P = 8$ GPa (the total compression is about 4% in volume), we obtain a practically unchanged gap, while LDA yields a band overlap of about 100 meV, similar to the experimental change of the semiconducting gap (from ~ 70 meV to < 0). Thus, LDA correctly reproduces the gap variation under pressure, but, as usual, consistently underestimates the gap (by ~ 70 meV). Moreover, the fact that the charge ordering and, presumably, the antiferromagnetism persist beyond the metal-insulator transition pressure, $P \sim 6$ GPa, sits well with the band picture. Finally, the nonmonotonic behavior of the resistivity in the crossover region, metallic at low T and semiconducting at high T , again agrees with the band character of the metallization.

Thus, using the pressure dependence of the resistivity as a litmus test for Mott-Hubbard behavior, we show that even the mostly correlated rare-earth nickelates, YNiO₃ and LuNiO₃, are not real Mott insulators, but rather are in a crossover regime closer to the itinerant side. Our first principle calculations explain quantitatively or semiquantitatively all unusual properties of this system: charge disproportionation, metal-insulator transition under pressure, pressure dependence of the Néel temperature. The main physics can be summarized as follows: (i) These materials are orbitally degenerate (JT), but lifting the orbital degeneracy via the traditional JT mechanism is not possible because of the large bandwidth; for the same reason, however, this degeneracy can be lifted by charge disproportionation without invoking a penalty due to on-site Coulomb repulsion. (ii) The gap is formed between the empty e_g band of the weakly magnetic Ni and the fully occupied spin-up band of the strongly magnetic Ni. Under pressure, this gap closes in the standard semimetallic way, by opening hole and electron pockets. Charge segregation at that point does not change much and the system remains CO in the metallic state.

Besides the nickelates discussed above, the same mechanism seems to be operative in many other materials, e.g., in some ferrates: CaFeO₃ [13], Sr₃Fe₂O₇ [14], etc., that nominally contain JT Fe⁴⁺ ($t_{2g}^3 e_g^1$) ions but which instead

of a JT distortion segregate into Fe³⁺ ($t_{2g}^3 e_g^2$) and Fe⁵⁺ ($t_{2g}^3 e_g^0$) without orbital degeneracy. Failure to stabilize monooxide CrO with a JT Cr²⁺ presumably is due to the same reason (more localized CrF₂ does exist, and JT distorts). In terms of localization all these systems, including the hypothetical CrO, lie in a crossover region and are either bad metals or small gap semiconductors, in agreement with our proposed picture.

Thus the behavior of all such systems has much in common, and the general trend is as follows: For strongly localized electrons with an orbital degeneracy we have at low temperatures the usual OO with JT distortion, but upon approaching the Mott transition the band broadening leads to a suppression of the OO, and a novel intermediate phase with charge differentiation, or charge ordering can appear. And finally this CO would melt at still larger values of t/U , when the system would become a usual metal. This phenomenon can be observed in a large class of materials, especially those with small or negative charge-transfer gap.

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- [1] J. A. Alonso *et al.*, Phys. Rev. B **64**, 094102 (2001).
- [2] J. L. Garcia-Munoz *et al.*, Europhys. Lett. **20**, 241 (1992).
- [3] J. A. Alonso *et al.*, Phys. Rev. Lett. **82**, 3871 (1999).
- [4] U. Staub *et al.*, Phys. Rev. Lett. **88**, 126402 (2002).
- [5] M. T. Fernández-Díaz *et al.*, Phys. Rev. B **64**, 144417 (2001).
- [6] P. Blaha *et al.*, computer code WIEN2K, Technische Universität Wien, Austria, 2001; The cutoff parameter $RK_{\max} = 7$, with local orbitals and the augmented plane wave (APW) extension was used. For the local density approximation (LDA) + U approach we took $U = 5$ eV and $J = 1$ eV. For most self-consistent calculations 54 inequivalent k points in the fourfold Brillouin zone were utilized; meshes with up to ~ 1000 inequivalent points were used for testing and for analyzing the DOS. Gradient corrections were included in all calculations.
- [7] J. L. García-Muñoz *et al.*, Phys. Rev. B **69**, 094106 (2004).
- [8] J. B. Torrance *et al.*, Phys. Rev. B **45**, 8209 (1992).
- [9] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **69**, 153105 (2004).
- [10] G. Demazeau *et al.*, J. Solid State Chem. **3**, 582 (1971).
- [11] J.-S. Zhou *et al.*, Phys. Rev. Lett. **95**, 127204 (2005).
- [12] R. Lengsdorf *et al.*, J. Phys. Condens. Matter **16**, 3355 (2004).
- [13] M. Takano *et al.*, Mater. Res. Bull. **12**, 923 (1977).
- [14] K. Kuzushita *et al.*, J. Phys. Soc. Jpn. **69**, 2767 (2000).
- [15] M. Amboage, Ph.D. thesis, Universidad del País Vasco, Bilbao, Spain, 2003.