Formal Valence, 3d-Electron Occupation, and Charge-Order Transitions

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While the formal valence and charge state concepts have been tremendously important in materials physics and chemistry, their very loose connection to actual charge leads to uncertainties in modeling behavior and interpreting data. We point out, taking several transition metal oxides (La2VCuO6, YNiO3, CaFeO3, AgNiO2, V2O5) as examples, that while dividing the crystal charge into atomic contributions is an ill-posed activity, the 3d occupation of a cation (and more particularly, differences) is readily available in first principles calculations. We discuss these examples, which include distinct charge states and charge-order (or disproportionation) systems, where different “charge states” of cations have identical 3d orbital occupation. Implications for theoretical modeling of such charge states and charge-ordering mechanisms are discussed.

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Spin ordering, and often orbital ordering, is normally unambiguous, as these properties are subject to direct observation by magnetic and spectroscopic measurements, respectively. Charge ordering (CO) and the actual charge of an ion is rarely measured directly, and the formal charge of an ion in the solid state can be a point of confusion and contention. Valence, oxidation number, and formal charge are concepts borrowed from chemistry, where it is emphasized they do not represent actual charge [1,2] and have even been labeled hypothetical [1]. As the interplay between spin, charge, orbital, and lattice degrees of freedom becomes more closely watched [3] and acknowledged to be a complex phenomenon, disproportionation and CO have become entrenched as the explanation of several high profile metal-insulator transitions (MIT). The possibility that CO in the charge transfer regime is associated with the oxygen sublattice, with negligible participation of either V and Cu, strong Cu spin-half moments reduced by hybridization with O 2p orbitals. The other configuration is the nonmagnetic state brings to mind. 3d cations, in their various environments and charge states, have maxima in their spherically averaged radial density ρ(r) in the range 0.6–0.9 a.u. At this short distance from the nucleus, the only other contribution to the density is the core contribution, which can be subtracted out and is unchanged during chemical processes or CO. Most relevant to the understanding of CO-driven transitions and disproportionation is the difference in 3d occupations Δn_d, which is given directly, without any integration, by the difference in the radial 3d densities at their peaks, where there are no competing orbital occupations to confuse charge counting. This specifically defined 3d occupation difference provides a basis for building a faithful picture of CO and of characterizing formal valence differences more realistically. We consider our computational results [6,7] for a selection of systems, then discuss some of the implications.

La2VCuO6 (LVCO) is a double perovskite compound providing a vivid and illustrative example. Our earlier study [8] revealed two competing configurations for the ground state. Using conventional identifications, one is the V4+ d3, Cu2+ d9 magnetic configuration (with bands shown in Fig. 1) identified as such because (i) there is one band of strong V d character occupied and one band of strong Cu d character unoccupied, and (ii) the moments on both V and Cu, 0.7 μ_B, are representative of many cases of spin-half moments reduced by hybridization with O 2p orbitals. The other configuration is the nonmagnetic d9 – d10 band insulator: all Cu d bands are occupied, all V d bands are unoccupied—a conventional ionic band insulator in all respects. The identification of formal valence (or oxidation state) is crystal clear.

The radial charge densities of V and of Cu for both configurations reveal an unsettling feature: the actual 3d occupations n_d of each of these V and Cu ions are identical for both configurations, in spite of the unit difference in...
all of the moment. The difference of charge in the minority spin orbitals. Similarly for Cu, the 0
or less uniformly from all other (nominally unoccupied) occupations characterizes the Jahn-Teller distortion. The increase in charge of the minority \( d_{x^2-y^2} \) orbital, the majority-minority difference in charge density at their peaks.) Thus ions with no real difference in 3d occupation can behave as if they comprise charge states differing by unity. Changes in spin-orbital occupations \( n_{\text{spin}} \), which quantify spin, orbital, and charge differences between the two states, can be quantified by the LDA + U spin-orbital occupations. For the V \( d^1 \) \( d_{xy} \) (Jahn-Teller split) orbital, the majority-minority difference is \( n_{xy} - n_{xy} = 0.77 - 0.07 = 0.70 \), which accounts for all of the moment. The difference of \( n_{xy}(d^1) - n_{xy}(d^0) = 0.77 - 0.11 = 0.66 \) between \( d_{xy} \) and the other two \( t_{2g} \) occupations characterizes the Jahn-Teller distortion.

FIG. 1. Bands near the Fermi energy (band gap) in the \( d^1 - d^0 \) magnetic, nearly Mott insulating, configuration of La\(_2\)VCuO\(_6\). Top: the V \( d_{xy} \)-up band is JT- and correlation-split off from the other two \( t_{2g} \) bands and fully occupied. Bottom: the Cu fat bands for the same system, showing one unoccupied Cu minority \( d_{x^2-y^2} \) band that is JT- and correlation-split from the \( d_{xy} \) band. The other \( d \) bands fall outside this energy range.

FIG. 2 (color online). Radial charge density (upper curve) of YNiO\(_3\) for \( Pbnm \) Ni and \( P_{2_1}1/n \) Ni1 and Ni2, showing there is no difference at the peak, which reflects the 3d occupation of the ion; a small difference shows up near the sphere boundary. The spin decompositions give easily visible differences. The vertical lines at the bottom right indicate conventional \( \text{Ni}^{4+}, \text{Ni}^{3+} \), and \( \text{Ni}^{2+} \) ionic radii, which have no relation to the (unvarying) 3d occupation.

We look at additional cases before addressing some of the implications.

Rare earth (\( \mathcal{R} \)) nickelates \( \mathcal{R}\text{NiO}_3 \) display a first order structural and MIT of great current interest. The \( Pbnm \) (GdFeO\(_3\) structure) \( \rightarrow \) \( P_{2_1}1/n \) transformation results in a large Ni\(_1\)O\(_6\) and a small Ni\(_2\)O\(_6\) octahedron, with Ni-O distances of 2.015 ± 0.015 and 1.915 ± 0.025 Å, respectively, that are not otherwise strongly distorted; see the inset of Fig. 2. At a temperature that varies smoothly from 600 to 300 K with increasing \( \mathcal{R} \) ionic radius, the resistivity of these nickelates changes sharply [9,10]. We focus on YNiO\(_3\); with its small ionic radius, it is one of the more strongly distorted members, and the resulting narrowed bandwidths make it more prone to strong correlation and CO tendencies [5]. Structural changes at the MIT have been studied extensively [9,11–14], which together with x-ray absorption spectral splittings [15–17] have been
interpreted in terms of charge disproportionation (or CO) \(2\text{Ni}^{3+} \rightarrow \text{Ni}^{1+\delta} + \text{Ni}^{3-\delta} \), with \(\delta = 0.3\) for \(\text{YNiO}_3\) [15].

This MIT in the nickelates has been recognized as paradigmatic by theorists. Mizokawa et al. modeled this system [18] with a multiband Hartree-Fock model in the charge-transfer regime and found evidence for CO on the oxygen sublattice for larger \(R\) cations, but concluded that \(\text{YNiO}_3\) was representative of a CO transition on the Ni sites. Mazin et al. [5] surveyed the competition between Jahn-Teller distortion of the \(d^3\) ion and CO and also concluded that \(\text{YNiO}_3\) is a prime example of a CO \(d^6 + d^8\) system. Lee et al. have investigated [19] a two band model for this system with a CO interaction in mean field, emphasizing CO effects. On the other hand, Yamamoto and Fujiwara [20] reported a very small (~0.03\(e^-\)) density functional based charge difference.

For the assumed (for simplicity) ferromagnetic order the calculated Ni1 and Ni2 moments are 1.4 and 0.65\(\mu_B\), respectively, for \(\text{YNiO}_3\) and several other members of this class, so these values are not sensitive to the magnitude of the distortion. They coincide with the values obtained from neutron diffraction [11], 1.4(1) and 0.7(1)\(\mu_B\), respectively, in the magnetically ordered phase. It is intriguing that the same moments were obtained in fully relaxed LaNiO3/LaAlO3 monolayer superlattices [21].

The 3\(d\) occupations, obtained as above directly from the maximum in the radial charge density plots in Fig. 2, are identical for Ni1, Ni2, and the single Ni site in the high temperature phase: there is no 3\(d\) charge transfer, or disproportionation, across the transition. The majority and minority radial densities and integrated charges of course differ (see Fig. 2) as they must to give the moment, but the total 3\(d\) occupation is inflexible. This constancy of the 3\(d\) occupation across the transition, and equality for Ni1 and Ni2, is inconsistent with microscopic disproportionation.

To illustrate the spin-orbital spectral density redistribution, the projected densities of states are shown in Fig. 3. All \(t_{2g}\) states are filled and irrelevant. The \(e_g\) spectral distribution is nonintuitive: weight from \(-5\) eV spin-down is transferred to \(-1\) eV spin-up. The majority \(e_g\) states just below the gap are strongly Ni1 in character, while the unoccupied bands just above the gap are primarily Ni2. Such behavior is expected for different charge states, similarly to the behavior in LVCO above; however, the total 3\(d\) occupation is identical.

The main differences between Ni1 and Ni2 show up in the unoccupied \(e_g\) states: the Ni1 spin splitting is 3.5 eV, a reflection of the on-site repulsion that opens the Mott gap in the majority \(e_g\) states, rather than Hund’s exchange splitting. The origin of the Ni2 moment is murky, not identifiable with any occupied spectral density peak. Note that in a Ni\(^{2+}\) + Ni\(^{4+}\) CO picture, Ni2 would be nonmagnetic. Not only is this calculated behavior not consistent with a CO picture, it involves redistribution not accounted for in any simple model. In spite of identical 3\(d\) occupations, the Ni1 and Ni2 core energies differ by up to 1.5 eV.

CaFeO\(_3\), another perovskite that displays the same \(Pbnm \rightarrow P2_1/n\) structural change at \(T_{MI}\) as the nickelates, is also explained [22] in CO language that invokes the unusually high (penta)valent state Fe\(^{5+}\). Analogously to \(\text{YNiO}_3\), we obtain identical 3\(d\) occupations for Fe1 and Fe2 ions. Quantum chemical embedded cluster calculations [23] and LDA + U studies [24–26] had noted that the Fe charge in both “disproportionated” sites differed little, but neither quantified the occupation as we have for \(\text{YNiO}_3\) and CaFeO\(_3\). The pentavalent state of Fe has most often been identified from Mössbauer isomer shift data, but Sadoc et al. [23] concluded the difference in isomer shift is primarily a measure of the covalency (Fe-O distance) rather than any real charge on Fe.

AgNiO\(_3\), a triangular, magnetically frustrated lattice compound with nominal Ni\(^{3+}\) ions, undergoes a structural transition at 365 K although remaining metallic [27–30]. Three inequivalent Ni sites arise, with a high spin Ni1 ion in an enlarged octahedron and two low spin Ni2, Ni3 = Ni2,3 ions in small octahedra. Based on the structural changes (which were quantified in terms of bond valence sums), the magnetic moments, and resonant x-ray scattering that confirms a calculated \(-1\) eV difference in core level energies between Ni1 and Ni2,3, this transition has been welcomed as the first realization of such a highly unusual \(3e_g^1 \rightarrow e_g^0 + 2e_g^{0.5}\) type of CO. Furthermore, using the charge difference per unit core level splitting of 0.66 eV led to an inferred charge disproportionation of \(-1.65e^-\), i.e., Ni1\(^{2+}\) + 2Ni2, 3\(^{3.5+}\). We have reproduced several of the first principles results [27,30] that were
used to support CO. The calculations give a large moment (> 1 \(\mu_B\)) on high-spin Ni\textsubscript{1} and very weak moments (≈ 0.1 \(\mu_B\)) on low-spin Ni\textsubscript{2},2 ions. We find, as in the cases above, that \(n_d\) for the three sites are identical. Moreover, our calculated core level differences, 0.6–0.8 eV, are roughly consistent with reported values \([30]\) (≈ 1 eV).

\(V_3O_7\) represents another oxide currently explained by a CO-driven MIT. It is structurally more involved, but first principles calculations of moments and geometries again have produced several results corroborating the experimental data \([31,32]\) and were used to support CO into \(V^{3+}\) and \(V^{4+}\) charge states on specific sites. As in the instances above, we find no differences in \(n_d\); the occupations are indistinguishable. The site energy differences, measured by differences in 1s, 2s, 2p core levels, differ by 0.9–1.2 eV for two sites, similar to the nickelates. The interplay of orbital order, structural distortions, and possible spin-singlet formation of half of the V ions provide a rich array of degrees of freedom, which can operate without need for disproportionation.

**Implications.**—We have established that, for several instances of CO transition systems as well as for the two self-evident charge states of LVCO, there is no difference in the 3d occupations for the different charge states that have been used to categorize their behavior. Such identification is possible because a choice of a region for integration is avoided; the peak charge region rather than tails of orbitals are used in the identification. This finding of constancy sharpens several reports of “small charge differences” between differing charge states (viz., Luo et al. \([33]\) for doped manganites; Haldane and Anderson \([34]\) in a multiorbital Anderson model, and Raebiger et al. \([35]\) from DFT calculations for TM impurities in semiconductors; Yamamoto and Fujiwara \([20]\) and also Park et al. \([36]\) for nickelates).

We see two primary implications: (i) the conceptual basis underlying a substantial aspect of transition metal physics is misleading, and (ii) modeling of structural and electronic transitions has, at least in several conspicuous cases, incorporated the wrong mechanisms by invoking inactive degrees of freedom. Actual cases of CO very likely do exist, but the burden of proof has shifted.

For these CO systems, the constancy of \(n_d\) suggests that \(U_d\) is too large to allow change in occupation \(n_d\) in or near the ground state (in the cases we discuss, and similar ones). In insulators the charge is more physically pictured in terms of (fully occupied) Wannier functions (WFs) than in terms of ambiguous populations of atomic orbitals, making them appear to be inviting. However, WFs are far from unique and, like molecular orbitals, WFs contain charge that cannot objectively be assigned to one atom or another, so a WF viewpoint is not promising.

A broader implication is that modeling of coupled structural and electronic transitions in terms of charges \([5,19]\) from atomic-like orbitals must be treated with caution: charge fluctuations in these systems are too high in energy to comprise a relevant degree of freedom. The important energy differences are characterized in terms of differences in hopping amplitudes, anion-cation distances, and (not recognized in most models) resulting changes in site energies, as well as very important Hund’s rule energies. Models that try to parametrize (for example) Ni\textsubscript{1}–Ni\textsubscript{2} differences by on-site charge will not be treating the relevant microscopic degrees of freedom. CO on the oxygen sublattice \([4,5]\) may also be problematic.

Charge states of ions serve to specify the occupations of spin orbitals. The essential degrees of freedom in determining this popular characterization, which professes to be quantitative, are the spin-orbital occupations, not as determined from the (real) density matrix but rather from the site symmetry, crystal symmetry, and the local moment. The LVCO example illustrates vividly how two different charge states, for both highly charged V and moderately charged Cu, can be represented by integer occupation of different numbers of orbitals while there is no change in \(n_d\). The concept of charge state projects onto integrally occupied orbitals, while the distribution of real charge is strongly nonintegral and often nonintuitive. These projections are backed up by the number of occupied spin-polarized bands (an integer), by the (discrete) local symmetry (JT distortion), by the local moment (with its quantization smeared by hybridization), and by the atomic radii, but each one of these characterizations is extremely flexible with a given amount of 3d charge.

More specifically to CO systems, the ionic environment in the high symmetry phase requires closer scrutiny. In both the nickelates and in \(V_3O_7\) there is evidence of distinct metal sites above the transition, in the (on average) symmetric phase, and the structural similarities of CaFeO\textsubscript{3} to RNiO\textsubscript{3} suggest similar behavior there. For nickelates, x-ray absorption spectra \([16,17]\) reveal that local signatures of Ni\textsubscript{1} and Ni\textsubscript{2} sites persist continuously across the MIT, and both sites also remain when driven across the phase boundary by pressure \([37]\). As we have shown, the coordination alone (i.e., with identical \(n_d\)) accounts for on-site energy differences of ≈ 1 eV in spectra that have often been used to support disproportionation. The MITs in some of these materials may be primarily order-disorder type; the onset of long-range order in nickelates results in carrier localization and gap formation, ergo a MIT but one due to structural order rather than CO.

We propose therefore that charge order should be used as the name, hence the interpretation, of a phase transition only if an objective, relevant charge difference is the likely mechanism; otherwise, the underlying mechanisms should be identified. Formal developments may be useful; for example, Jiang et al. have provided a specification \([38]\) of integer charges in an insulator that they propose as oxidation states (which are identical to charge states in metal oxides.) Based on integration over a configuration space
path of the dynamic Born effective charge, their expression assigns (in principle) an integer charge to each atom in any insulator. Notably, their specification does not refer to $3d$ charge explicitly and furthermore depends explicitly on dynamical effects (electron response to ion motion). Also, many CO interpretations only hold water if the supposed charge difference $\pm \delta$ is much smaller than unity ($\delta \sim 0.3$ for the nickelates). More experience will be needed to learn how best to interpret their definition.

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[6] The density functional based linearized augmented plane wave code WIEN2K [7] has been used in our calculations, where we have applied correlation corrections (LDA + U) as is usually necessary to describe 3$d$ oxides. Computational methods are as described in Ref. [8].