Formal Valence, d Occupation, and Charge-Order Transitions

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While the formal valence concept has been tremendously important in materials physics, its very loose connection to actual charge leads to difficulties in modeling its consequences and interpreting data correctly. We point out, taking several transition metal oxides (La_2VCuO_6, $YNiO_3$, $CaFeO_3$, $AgNiO_2$, V_4O_7) 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 transitions are discussed.

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