Quantifying charge ordering by density functional theory: Fe₃O₄ and CaFeO₃


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We demonstrate that charge ordering can be quantitatively predicted by analyzing the Born effective charge (BEC), resolving the long-standing discrepancy between first-principles charge analysis and the nominal concepts of charge disproportionation in Fe₂O₄ and CaFeO₃. In particular, the BEC differences between the disproportionated Fe ions are calculated to be ~2e, being in excellent agreement with the nominal charge separation in CaFeO₃ while suggesting the charge disproportionation in Fe₂O₄ is understood by the charge separation ~2e instead of the nominal separation of ~1e.

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Simple concepts have the power to guide us to understand many scientific phenomena even when they are incomplete initially [1]. In this context, the oxidation state/number is undoubtedly one of the most successful examples in the development of inorganic chemistry. Enormous success has been seen for the phenomenological usages of the concept in interpreting, understanding, and predicting many chemical phenomena for centuries. However, when the quantitative values are compared, it seems that few direct first-principles charge analyses can lend the support to concept. A classical illustration has been given recently by Raebiger et al. [2] who specifically studied multiple-charge configurations of isolated transition metal atoms in representative host materials in terms of oxidation state change. In complete contrast to the ionic picture, i.e., the oxidation numbers of the transition metal atoms should have changed in the scale of a few electrons, Raebiger et al. found by their first-principles analysis that the total charge around the transition metal atoms were kept almost unchanged despite the oxidation state having been altered.

The problem is even evidenced in the case of charge ordering [3–10] by which a cation in the parent lattice site is evolved into two or more charged species with different oxidation states, leading to an ordered superlattice and charge disproportionation. Charge ordering mostly occurs in strongly correlated transition metal oxides such as magnetite Fe₃O₄ [3–6] perovskite manganese oxides, [7,8] ferroelectric frustrated LuFe₂O₄ [9] CaFeO₃ [10] and some quasi one-dimensional organic conductors. [11] In particular, the charge ordering of magnetite Fe₃O₄ has been an open question for decades, from the observation of Verwey transition [4] to many recent theoretical attempts [12–16] and the most recent experimental determination [6] of its crystal structure of the low temperature phase. At room temperature, Fe₂O₄ crystallizes in the inverted cubic spinel structureFd3m. In terms of oxidation state, room temperature Fe₂O₄ has been modeled with the tetrahedral A sites occupied by Fe³⁺ cations whereas octahedral B sites are occupied by an equal number of randomly distributed Fe²⁺ and Fe⁵⁺ cations. Verwey [4] discovered that Fe₂O₄ undergoes a sharp first order transition on cooling below 120 K, and the structure distorts from the cubic symmetry. The transition was explained by a charge ordering of the Fe²⁺ and Fe⁵⁺ states on the B sites in alternating layers. However, most of the first-principles calculations [12–15] predict the charge difference between the two ionic states on the B sites in Fe₂O₄ to be as small as 0.2e, far less than the nominal ionicity difference of 1e between the two states. Mulliken net charge populations do not correct the problem either [15].

In this Letter, we resolve the discrepancy by computing the dynamical Born effective charge, showing that the Born effective charge itself can quantitatively manifest the charge ordering. The Born effective charge is a widely adopted physical quantity for studying ionic crystals, leading to amazing agreements with measurements for the calculations of the spontaneous polarization as well as the phonon frequency differences between the longitudinal optical (LO) and the transverse optical (TO) phonon modes [17–22]. It defines the atomic charges in terms of the change of the dipole moment or polarization of an ionic crystal with respect to electric perturbations. [23] Most important, the Born effective charge is a well formulated quantity in the ab initio framework [18,24,25] that can be calculated without any ambiguity.

To calculate the Born effective charge, we employed the linear-response theory implemented in the Vienna ab initio Simulation
Package (VASP, version 5.2) by Gajdoš et al. [26] together with the projector-augmented wave (PAW) method [27,28]. For the Fe-free materials, the local density approximation to the exchange–correlation functional (according to Ceperley and Alder as parameterized by Perdew and Zunger [29]) was employed in all calculations. For FeO₃ and CaFeO₃ due to the strong correlation among the Fe 3d electrons, we employed the rotationally invariant DFT + U method by Liechtenstein et al. [30] together with the Perdew–Burke–Ernzerhof (PBE) [31] exchange–correlation functional and Ca [33p4s], Fe [3p3d4s], and O [2s2p] electrons being treated in valence states. We have chosen to use $U = 5$ eV and $J = 1.0$ for the $d$ orbital of Fe. We also did test calculations using $U = 4.5$ eV and $J = 0.89$ eV and find that this does not make the main conclusions of the present work.

For FeO₃, we start from building an initial 56-atom supercell which is in shape similar to the one most frequently adopted structure [32] in the published literatures [12,14,33,34], based on the cubic spinel structure of Fd3m. Then the lattice symmetry and atomic positions as well as the cell volume are all allowed to relax to get the lowest energy structure. All the Fe atoms at the A sites are treated as spin down and those at B sites are treated as spin up to mimic the ferromagnetic nature of FeO₃ at low temperature. Total energy calculations have been performed at six fixed volumes near the equilibrium volume with volume increment of ~5% while both the lattice shape and atomic positions are allowed to relax. The final equilibrium lattice properties are derived by fitting the calculated energy–volume data using the modified 5-parameter Birch–Murnaghan (mBM5) equation of state [35]. The derived fitting error is around $~10^{-5}$ eV, justifying a good convergence. The total energy is $-6.93451$ eV/atom and the bulk modulus is 160.67 GPa. Being compared with the measured lattice parameters of $a = 6.94437$ Å, $b = 5.92471$ Å, and $c = 16.77512$ Å of Wright et al. [5], the calculated values are 6.01212, 6.01075, and 17.11357 Å, respectively, which represent the overestimations of ~2%, typically for DFT calculation with PBE functional for oxides.

Since CaFeO₃ is more complicated due to the rather complex magnetic structure, we limit the calculation to at the experimental volume to search the lowest energy structure with both the lattice shape and atomic positions being allowed to relax. We start from a searching from the all possible 158 40-atom supercells spanned from the pbnm 20-atom structure [36]. It turns out that the lowest energy structure is a double layer antiferromagnetic structure along the long axis direction as shown in Figure 1b. The total energy for the lowest energy structure is $-6.55109$ eV/atom. Being compared with the measured lattice parameters of $a = 5.31182$ Å, $b = 5.34775$ Å, and $c = 7.52058$ Å of Woodward et al. [37] at 15 K, the calculated values are 5.30598, 5.35454, and 7.51841 Å, respectively, after converting the 40-atom double layer antiferromagnetic lattice into the pbnm 20-atom structure.

Magnetite FeO₃ is the parent compound for many magnetic materials such as spinel ferrites and represents a mixed-valence system. Most of the previous first-principles calculations [12–16] show that the charge difference between the two B site Fe ions is far less than the nominal ionic charge difference of 1e between the Fe³⁺ and Fe²⁺ ions. For the convenience of discussions, in the following we will use the indexing symbol given by Wright et al. [5] in their Fig. 2 for the Fe positions in the B sites. For the typical numerical values published in the literature about the Fe valences for FeO₃, the calculations of Jeng et al. [12] show that the charges of Fe are 2.43e, 2.59e, 2.56e, and 2.42e for the B1, B2, B3, and B4 sites, respectively, while the Mulliken net charge populations of Rowan et al. [15] show that the charges of Fe are 2.10e, 2.10e, 1.83e, 2.17e, 2.11e, and 1.81e for the A1, A2, B1, B2, B3, and B4 sites, respectively.

The results of our study on charge disproportionation in FeO₃ are summarized in Table 1 and plotted in Figure 1a. In Table 1, for the convenience of discussion, we also have a column with heading of ‘dynamical charge state’ whose data are derived by truncating the values under the heading $Z$ which represents an average over the diagonal components of Born effective charges.

For the B sites, according to the column with heading $Z$, we find that the charge separations are about 2e, doubling the nominal value of 1e. It is even more surprising to note that the calculation shows that the B sites are made of Fe cations with $+$ and $+$ charges according to the column with heading ‘dynamical charge state’, being different from the assumed nominal Fe³⁺ and Fe²⁺ charge states. The present calculation shows that certain B sites are 1e more charged than the A sites which are assumed to be highest charge positions (i.e., occupied by the nominal Fe³⁺ ions) according to the Verwey model. Mulliken analyses by Rowan et al. [15] also show that certain Fe ions (B2 and B3) in the B sites are more charged than the atoms in A sites.

The calculated charge distribution pattern among the Fe B sites (see Figure 1a) is closer to the class II model (Fig. 2 in the work of Wright et al. [5]) than the class I model proposed by Wright et al. [3,8]. The frequently employed class I model [12–15] assumed that B1 and B4 Fe ions are electron-rich while B2 and B3 Fe ions are electron-poor. Our results show that all the four B sites can be mixtures of electron-rich and electron-poor Fe ions. Charge ordering is also shown for the oxygen atoms, supporting the recent experimental analysis by Huang et al. [34].

The next prototype studied in the present Letter is CaFeO₃, which shows a transformation of the crystal structure accompanied with a change in the electrical properties upon the change of temperature. By the $^{57}$Fe Mössbauer spectrum, Takano et al. [10,39] observed that the single line found at high temperature is split when the temperature is lowered, which has been interpreted from the two different isomer shift values as a transition from a non-charge-disproportionated phase, containing equivalent Fe⁴⁺ ions, to a charge-disproportionated phase containing Fe³⁺ and Fe⁵⁺ ions [40].

The results of our study on charge disproportionation for CaFeO₃ are depicted in Figure 1b and summarized in Table 2 in which the results of Bader analysis [41] are also included. It is evident from the Bader analysis that one can hardly see even a trace of charge disproportionation. Several important observations can be made:

First, the nominal charge separation of 2e between the Fe ion states is precisely predicted by the present calculations. Further, the calculated dynamic atomic charges of Fe ions are ~1.5e larger than their nominal oxidation number. Here we may reiterate that the calculated Born effective charges are more reasonable for the precise predictions of the LO–TO splitting for phonon frequencies of the ionic materials [17–22]. Finally, after rounded up to integers (see the column with heading ‘dynamical charge state’ in Table 2), it is found that dynamical charges of the two Fe cations are $+$ and $+$ for the charge-disproportionated phase of CaFeO₃.

For both FeO₃ and CaFeO₃, the present calculations show that the averaged Born effective charges of the Fe ions are roughly 1e larger than the nominal Fe oxidation numbers in the corresponding compounds. To further support the calculations, we collect in Table 3 the calculated Born effective charges for a range of ionic materials. We see from Table 3 that the averaged Born effective charges for most of the compounds (listed as ‘regular’) are comparable to the nominal oxidation numbers, though they do not show integer charges. For the ‘irregular’ materials listed Table 3, the calculated averaged Born effective charges show larger deviations from the nominal ionic states. These materials are either coordination compounds, or contain titanium, or demonstrate exotic properties such as superconductivity or negative thermal expansion. Looking through Table 3, one could raise the question why the calculated Born effective charges do not manifest as...
integers and why larger deviations from the nominal ionic values are seen for the irregular compounds. One answer can be found in the previous work (mainly for the $\text{ABO}_3$ perovskite compounds) by Ghosez et al. [42] in terms of the static and dynamical atomic
charges. Furthermore, there are also covalent bonding interactions [42,43] which are rather directional and can either enhance or weaken the Born effective charges.

In conclusion, we show that the charge ordering in Fe$_3$O$_4$ and CaFeO$_3$ can be precisely predicted under the framework of first-principles calculation by means of the Born effective charges, circumventing the difficulty in dividing the electronic charge into the atomic contributions. For both Fe$_3$O$_4$ and CaFeO$_3$, the present calculations show that the averaged Born effective charges of the Fe ions are roughly 1e larger than the nominal Fe oxidation numbers.

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