Comment on “Charge order in Fe_2OBO_3 : An LSDA+U study”

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In a recently published paper [Phys. Rev. B **72**, 014407 (2005)], Leonov *et al.* present an LSDA+U study of the low temperature monoclinic structure of the iron oxoborate (Fe_2OBO_3). They report on Fe^{2+} - Fe^{3+} charge ordering without taking into account recent resonant x-ray scattering experiments, which demonstrate the lack of charge ordering in a closely related oxide such as Fe_3O_4 . They propose that the charge ordering occurs between equivalent crystallographic sites. First, this result, apart from surprising, is at odds with basic concepts in condensed matter. Second, we argue on the reliability of this theoretical approach, showing that a strong discrepancy is obtained for the calculated total and d -projected charges at Fe atoms with formally the same valence state and local environment between two closed related compounds, Fe_3O_4 and Fe_2OBO_3 , using the same theoretical method. Finally, we reconsider the reported theoretical calculations on the basis of a rigorous definition of the concepts of charge and orbital ordering and we show that Fe_2OBO_3 does not show charge ordering.

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Electronic localization in transition metal (TM) oxides has continuously been a matter of debate from the beginning of modern investigation. The most widely accepted theory to explain the breakdown of the Bloch band theory, giving rise to conduction in TM oxides derived from Mott's ideas.¹⁻³ This model supports two basic ingredients in the description of the electronic properties of TM oxides; (i) d electrons are considered as localized at the TM atoms and (ii) due to this strong localization, the intra-atomic Coulomb repulsion (U) is considered the relevant parameter. However, these ideas enter in conflict with formally mixed valence TM oxides where two different d^n , d^{n+1} valence states occur. The formal valence of the TM atom has a noninteger value in these oxides so its electronic configuration should be defined as $d^{\text{noninteger}}$. This fractional occupation of the d orbital is in clear contradiction with Mott's ideas of strong d -localization and intra-atomic Coulomb repulsion. In order to overcome this incongruity maintaining Mott's theory, there are two possible solutions either a temporal or a spatial separation. Within the first, the electronic configuration of the TM atom is described as fluctuating between two integer d -electronic configurations, in such a way that the “mobile” electron expends nearly all the time in one configuration, the hopping time from this configuration to the other being long. This is called a fluctuating mixed valence compound. The other possibility is that the two integer d -electronic configurations freeze in the lattice. In such a way, the mixed valence compound is described as a mixture of two ions with different formal valence states, i.e., inhomogeneous mixed-valence state. When the two different valence states localize in an ordered way in the lattice, we call it a charge ordered (CO) phase.⁴

These concepts were contained in the classical description of the Verwey transition in magnetite.^{5,6} Above the Verwey transition temperature (T_V), the octahedral Fe atoms fluctuate between Fe^{2+} ($3d^6$) and Fe^{3+} ($3d^5$) integer electronic configurations while below T_V , the mobile electrons belonging to Fe^{2+} and Fe^{3+} ions order themselves over octahedral sites

in the lattice. The transition is described as an electronic order-disorder phase transition and it supplies a simple and elegant explanation to the discontinuous change in the electrical conductivity that occurs at the phase transition. Despite that the experiments ruled out in the Verwey CO pattern, all attempts to construct a refined CO model set failed and a lot of experimental facts point out against the CO conception, itself (see Ref. 7 for a critical revision of the Verwey transition), the question of CO in magnetite still survives. Our complete resonant x-ray scattering (XRS) studies in magnetite demonstrate the lack of CO at the octahedral Fe sites.⁸⁻¹⁰ In particular, it resolves definitely the controversy on the possible CO with [001] and [001/2] periodicities.¹⁰ If it exists, the charge disproportionation must be very small [lower than 0.1 e^- and 0.05 e^- for the (001) and (001/2) periodicities, respectively]. We only pay attention to two important conclusions of the XRS experiments in magnetite regarding the description of its electronic structure: (i) the interaction time is extremely short, about 10^{-15} sec, so the electron is shared among different octahedral Fe atoms in times lower than this one and (ii) the observed trigonal anisotropy of the octahedral sites in both, magnetite^{8,9} and spinel ferrites.¹¹ Some resonant x-ray diffraction experiments on magnetite have also remarked on charge segregation along the c axis but their analysis is far from convincing, the anomalous scattering factor was treated as a scalar instead of a tensor.¹²⁻¹⁴ Recently, a small charge disproportionation was also proposed for a $\text{Fe}_3\text{O}_4/\text{MgO}$ sample.¹⁵ On the other hand, oxygen K edge XRS spectra indicate that the charge modulation occurs on the oxygen atoms instead of the iron ones.¹⁶ In addition, previous theoretical studies by Szotek *et al.*¹⁷ indicate that this possible charge disproportionation is not of an electronic origin but determined by the structure. By electronic structure calculations using the LDA+U method Madsen *et al.* also obtained a charge disproportion along the c -axis in the monoclinic structure of Fe_3O_4 (Ref. 18).

The paper of Leonov *et al.*¹⁹ applies the same LSDA+U method recently used for the low temperature monoclinic

TABLE I. Comparison between total and l -projected charges and magnetic moments for inequivalent Fe atoms in the low temperature phases of Fe_2OBO_3 and Fe_3O_4 taken from Refs. 14 and 15, respectively.

Fe ion	Sample	q	q_s	q_p	q_d	q_d ($\text{Fe}^{3+}/\text{Fe}^{2+}$)	M (μ_B)	M ($\text{Fe}^{3+}/\text{Fe}^{2+}$) (μ_B)
$\text{Fe}(\text{B}_1)^{2+}$	Fe_3O_4	6.04	0.17	0.19	5.69	6	3.50	4
$\text{Fe}(\text{B}_4)^{2+}$	Fe_3O_4	6.03	0.16	0.18	5.69	6	3.48	4
$\text{Fe}(1)^{2+}$	Fe_2OBO_3	7.12	0.35	0.50	6.27	6	-3.65	-4
$\text{Fe}(2)^{2+}$	Fe_2OBO_3	7.04	0.34	0.50	6.21	6	3.69	-4
$\text{Fe}(\text{B}_2)^{3+}$	Fe_3O_4	5.73	0.19	0.21	5.44	5	3.94	5
$\text{Fe}(\text{B}_3)^{3+}$	Fe_3O_4	5.91	0.19	0.21	5.51	5	3.81	5
$\text{Fe}(1)^{3+}$	Fe_2OBO_3	6.90	0.40	0.55	5.95	5	-4.20	5
$\text{Fe}(2)^{3+}$	Fe_2OBO_3	6.79	0.38	0.54	5.86	5	4.33	5

structure of Fe_3O_4 (Ref. 20) to carry out a theoretical investigation of the electronic structure of the iron oxoborate (Fe_2OBO_3). The calculations were made using the $P2_1/c$ structure of the low temperature phase determined by Atfield *et al.*^{21–23} First, they conclude a very surprising result using the double ($2a \times b \times c$) supercell, which is that crystallographic equivalent sites Fe(1) and Fe(2) are nonequivalent from the electronic point of view, but Fe(1) and Fe(2) are split into $\text{Fe}(1)^{3+}$ and $\text{Fe}(1)^{2+}$ and into $\text{Fe}(2)^{3+}$ and $\text{Fe}(2)^{2+}$, respectively, in view of the authors. We argue to show that this is probably an overstatement. Regrettably, the authors only show the results for this double supercell though the simple unit cell is the one that reflects the experimentally refined structure. It is the first time, on our knowledge, that the crystallographic translational symmetry can be broken introducing only the intra-atomic Coulomb repulsion (U) term. Previous theoretical attempts to simulate the CO in magnetite have always needed the concurrence of an effective intersite Coulomb interaction to include the condition that octahedral Fe near neighbors could have a different charge.^{24–26} The crystallographic symmetry is normally the starting point for any of the approaches used in band theory so this result breaks a basic principle of solid state physics. As the electronic state of one atom only depends on the local geometry, even in the case of symmetry breaking by the magnetic ordering, the electronic states of structurally equivalent sites are always the same although the magnetic moment points to different directions. In other words, the electronic states (or the projected density of states) of structurally equivalent atoms must be the same, independent of use for the calculations, the simple or any multiples of the unit cell.

On the other hand, if crystallographic equivalent sites were not equivalent from the electronic point of view, as the authors propose, this result would have strong implications that the authors have not considered in detail. Let us now give an example. The bond valence sums (BVS) method correlates nearest interatomic distances with the valence state²⁷ and it works nicely. Following the author's claim, we have two Fe atoms with different valence states at crystallographic sites with the same nearest interatomic distances but also with the same local structure. It is straightforward to say that this claim is inconsistent with the result of an average 2.5+

value of valence of Fe atoms estimated by the experimental BVS method. Consequently, the supposed CO (or charge disproportionation) determined by BVS in a lot of compounds would be not justified as the method would not be reliable enough. We note that the same argument can be applied to other experimental techniques such as x-ray absorption spectroscopy or XRS, where the determined valence state is also directly related to the local structure.

Second, we compare the results of these LSDA+ U calculations between two semi-valence $\text{Fe}^{2.5+}$ closely related compounds, Fe_2OBO_3 and Fe_3O_4 . Table I reports total and l -projected charges and magnetic moments calculated for inequivalent Fe atoms in the low temperature ordered phase of the two samples, taken from Refs. 19 and 20, respectively. The strong discrepancy of 1 electron for the calculated total charge of Fe atoms with formally the same valence state, in assignment of the authors, between the two oxides is evident. Octahedral Fe^{2+} atoms have an averaged total projected charge of $q=6.035$ electrons in magnetite, whereas in Fe_2OBO_3 , this average total charge is $q=7.08$ electrons. The same can be said for the octahedral Fe^{3+} atoms, with $q=5.8$ electrons in Fe_3O_4 and $q=6.85$ electrons in Fe_2OBO_3 . A discrepancy is also observed for the calculated d -projected occupation. The obtained electronic configurations for Fe^{2+} and Fe^{3+} atoms in magnetite are $3d^{5.69}$ and $3d^{5.48}$, respectively, while they are $3d^{6.24}$ and $3d^{5.90}$ in Fe_2OBO_3 . We remember here that the atomic electronic configuration is $3d^6$ for Fe^{2+} and it is $3d^5$ for Fe^{3+} . We can derive several critical conclusions from this comparison: (i) The average interatomic distances for the octahedral Fe atoms are very similar for the two compounds, so it is not consistent that the calculated total and d -projected charges on the Fe atoms differ by about 1 electron and 0.5 electron, respectively, between the two samples. These strong differences between formally the same ionic states call into question the reliability of these calculations. (ii) The criteria for assigning an integer valence state 2+ or 3+ to specific Fe atoms is not justified except for obtaining a near bimodal distribution. In fact, the obtained total and d -projected charge is larger for Fe^{3+} in Fe_2OBO_3 than for Fe^{2+} in Fe_3O_4 . In particular, the d -projected charges for Fe^{2+} and Fe^{3+} in Fe_2OBO_3 are both very close to the $3d^6$ of the atomic Fe^{2+} .

Finally, Leonov *et al.*'s paper gives some arguments to make compatible the absence of experimental evidences of

CO in the low temperature phase, which merits discussion. They explicitly state that no long range $\text{Fe}^{2+}/\text{Fe}^{3+}$ ordering is directly observed by x-ray, neutron or electron diffraction. We note that a difference of about $0.5 \mu_B$ is obtained between the calculated magnetic moments for the Fe^{2+} and Fe^{3+} (see Table I). Differences of the same order of magnitude have been resolved from the refinement of neutron diffraction data, for instance in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (Ref. 28). In addition in this case, this difference in the magnetic moments of Fe^{2+} and Fe^{3+} should give rise to the observation of a magnetic reflection characteristic of this new periodicity. Moreover, they argue that the observed enlargement of the monoclinic distortion (β angle) below the transition temperature is originated by the CO scheme obtained from the LSDA+U calculations that destroy the mirror symmetry of the high temperature orthorhombic phase. They also argued that the a -axis periodicity should be increased by at least a factor two but this a doubling has not been observed.^{19,22} They try to justify the absence of insights for CO, hypothesizing that the lack of observation of long-range CO by diffraction is due to the very small CO domains and the superstructure peaks are too weak and broad to be observed. But we disagree with the authors on the fact that the long-range monoclinic lattice distortion was intimately correlated with the occurrence of CO. Both, superstructure peaks and increasing of the monoclinic distortion must be simultaneously observed because the correlation lengths for the monoclinic distortion and the CO must be the same. Thus, the smallness of the domains would also impede the observation of the monoclinic distortion if its origin were the CO.

The authors also cite two experimental facts as indirect insights of CO. Neither the small discontinuity in the electrical conductivity nor the strong change in the Mössbauer spectrum across the phase transition can be considered as a direct proof of CO as it is discussed in the recent critical review of the Verwey transition.⁷ Metal-insulator phase transitions, characterized by a discontinuity in the electrical resistivity, occur for different transition metal oxides,²⁹ including formal integer valence compounds. Moreover, the temperature dependence of the Mössbauer spectra clearly shows the onset of the so-called CO transition although Mössbauer spectroscopy cannot be considered as conclusive as the authors think. Let us comment on the case of the archetypical CO compound, Fe_3O_4 . The so-called CO transition is also clearly reflected in the Mössbauer spectra. However, an adequate model for the interpretation of the spectra recorded below T_V has not been found yet. The successive experiments and their different interpretations⁷ either in terms of CO of Fe^{2+} - Fe^{3+} cations or in terms of a delocalized electron model justify our previous statement.

From the above points, we reconsider here the LSDA+U results in Fe_2OBO_3 with respect to the concept of CO. As defined in the introduction, CO in this case would mean that Fe^{2+} and Fe^{3+} ions are periodically ordered in the lattice.^{3,6} This definition implies that the Fe d -states in Fe_2OBO_3 are localized and the electronic structures of these

Fe atoms must be well described as $3d^n$ with n as the integer. Moreover, the interpretation of the metal-insulator phase transition is based on this concept of CO. Above T_{CO} , the outer electron is jumping between different crystallographic sites and below T_{CO} , this electron is localized in the lattice in such a way that a periodic ordering of two valence states (i.e., $\text{Fe}^{2+}/\text{Fe}^{3+}$) is obtained.^{3,6} This description enters in conflict with the implicit theoretical approach used by Leonov *et al.*^{19,20} in their calculations. In those papers, the electronic structure of Fe_2OBO_3 is described in a band structure approach despite the Fe d states are considered localized. Thus, the metal-insulator phase transition is described as originated by the opening of a gap in the band structure at the Fermi level. This opening is generally driven by a structural phase transition, which cause the separation of the high temperature equivalent sites in different inequivalent sites. Consequently, a periodicity associated with these different crystallographic sites appears in the low temperature phase. It is obvious that the total and l -projected charges must be different for the inequivalent crystallographic sites, but the resulted projected charge disproportionation is generally very small. Calling CO to the periodic arrangement of different atoms with slightly different projected charges makes the classical concept of CO lose its physical meaning. As we commented before, $\text{Fe}^{3+}(\text{Fe}^{2+})$ in Fe_2OBO_3 is different from $\text{Fe}^{3+}(\text{Fe}^{2+})$ in Fe_3O_4 and those of $\text{Fe}^{3+}(\text{Fe}^{2+})$ are completely different from $\text{Fe}^{3+}(\text{Fe}^{2+})$ in integer valence iron oxides such as Fe_2O_3 or FeO where an integer d occupation is expected. In other words, the ordered entities are not well defined, so speaking of CO [here we extend this criticism to the concept of orbital order (OO)] of nondefined entities are completely meaningless.

Leonov *et al.* consider the $3d$ atomic orbitals as the basis functions of their band structure calculation. Within this approach, we can define an occupation of each of the $3d$ atomic orbitals and we can still speak in terms of charge or orbital ordering related to the noninteger occupation of these orbitals (note that these orbitals are not eigenvalues of the energy). However, it is then necessary to explicitly state that the ordered entities correspond to intermediate valence states far from the ionic ones. If not, any structural transition which differentiates crystallographic sites for the same atom that implies different charge projection or electronic symmetry on these atoms could be called CO transition. Moreover, site's occupations different from the bimodal one are always possible within this scheme and they also enter in dispute with the classical definition of charge/orbital ordering.

Despite all the previous considerations, Fe_2OBO_3 and Fe_3O_4 are clear examples of intermediate valence TM oxides. They show metal-insulator (semiconductor-semiconductor) phase transitions without the occurrence of a bimodal distribution of the projected charge onto the iron atoms in two different crystallographic sites. In particular, for Fe_2OBO_3 , equivalent crystallographic sites must support the same projected charge.

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