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Reply to "Comment on 'Spin- and charge-ordering in oxygen-vacancy-ordered mixed-valence $Sr_4Fe_4O_{11}$' "

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Recently, using density-functional theoretical calculations, we have reported [Phys. Rev. B **74**, 054422 (2006)] that formal Fe^{3+} ions reside at the square-pyramidal site and Fe^{4+} ions in the octahedral site in $Sr_4Fe_4O_{11}$. Based on the interpretation of experimental structural and Mössbauer data from the literature, Adler concludes that our previous first-principles results disagree with experiments on the assignment of oxidation states to Fe in the square-pyramidal and octahedral environments in $Sr_4Fe_4O_{11}$. From a critical examination of the structure data for $Sr_4Fe_4O_{11}$ and related oxides with Fe in different oxidation states and theoretically simulated Mössbauer parameters (hyperfine field, isomer shift, and quadrupole splitting), here we show that information on charges residing on the different constituents cannot be directly derived either from experimental structure or Mössbauer data. From additional analyses of the chemical bonding on the basis of charge density, charge transfer, electron localization function, crystal orbital Hamilton population, Born effective charge, and partial density of states, we substantiate our previous assignment of formal Fe^{3+} and Fe^{4+} to the square-pyramidal and octahedral sites, respectively, in $Sr_4Fe_4O_{11}$.

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Recently, using density-functional theoretical calculations, we reported[1] that formal Fe^{3+} ions reside at the square-pyramidal sites and Fe^{4+} ions at the octahedral sites in $Sr_4Fe_4O_{11}$. Based on the interpretation of experimental structure and Mössbauer data from the literature, Adler[2] concludes that our previous first-principles results disagree with the experimental findings with regard to the assignment of oxidation states to the Fe sites in $Sr_4Fe_4O_{11}$. In an attempt to disprove Adler's arguments, here we present a critical analysis of the "correlation" between charge state and bond length for iron-containing oxides as well as the outcome of theoretically simulated Mössbauer parameters. In order to further substantiate our previous findings, we have also made additional calculations to illuminate different aspects of the chemical bonding in $Sr_4Fe_4O_{11}$ and, thus, strengthen our conclusions. Owing to space limitations, more detailed analyses and discussions are provided in a subsequent paper.[3]

The crystal structure of $Sr_4Fe_4O_{11}$ comprises two nonequivalent iron atoms in equal amounts ($Fe1^s$ in square-pyramidal and $Fe2^o$ in octahedral coordination) and this constellation causes difficulties for the assignment of charge states as well as a detailed specification of the antiferromagnetic (AF) arrangement. The results from our theoretical calculations show that the $Fe1^s$ and $Fe2^o$ sites are occupied by (formally) Fe^{3+} and Fe^{4+}, respectively, with AF ordering of the $Fe2^o$ moments. We would like to specifically emphasize that this conclusion does not contradict the experimental results of Hodges *et al.*[4] and Schmidt *et al.*,[5] but rather the interpretation of the experiments with regard to the assignment of oxidation state for the two different Fe ions in Ref. 4 and the specification of which of the Fe ions exhibits long-range magnetic ordering in Ref. 5.

Hodges *et al.*[4] used a bond-strength model proposed by Ziólkowski[6] to assign the 4+ and 3+ oxidation states to the $Fe1^s$ and $Fe2^o$ sites, respectively. In simple oxides, the bond-strength sum around a given cation should exactly match its valence (z), whereas for multicomponent oxides, such sums are expected to be different from z.[6] Therefore, for a complex oxide such as $Sr_4Fe_4O_{11}$, individual bond-strength sums for crystallographically nonequivalent Fe ions may not be meaningful. So, Schmidt *et al.*[5] compared the bond-strength sums over all Fe sites of the unit cell derived using two different models; one with Fe^{3+} at $Fe1^s$ and Fe^{4+} at $Fe2^o$ sites, and vice versa. The calculated average sums per iron atom based on these alternatives are 3.37 and 3.47, respectively. As the difference is very small, it is meaningless to assign the oxidation states of $Fe1^s$ and $Fe2^o$ sites based on bond-strength considerations. Hence, Schmidt *et al.*[5] used chemical insight and crystal structure information for Sr-Fe-O compounds to arrive at the same conclusion as ours regarding the oxidation state assignment.

Let us first take an elementary chemistry viewpoint to analyze how the oxidation state of Fe would evolve upon the introduction of oxygen vacancies into the pristine $SrFeO_3$ lattice. It is generally accepted that Fe donates electrons and O accepts electrons in a Sr-Fe-O lattice. According to an ideal ionic picture and a fully oxygen-ordered system, Fe is surrounded by six oxygens in the 2− state. As Sr formally prefers the 2+ state, one can ascribe a formal charge of 4+ to all Fe ions in $SrFeO_3$. On the other hand, if one systematically removes one apical oxygen from alternate FeO_6 structural subunits of $SrFeO_3$, one obtains $Sr_4Fe_4O_{11}$ with an equal number of Fe in square-pyramidal ($Fe1O_5^s$) and octahedral ($Fe2O_6^o$) coordinations. As the local environment of the octahedra will be approximately the same as that in $SrFeO_3$, one would expect that the formal charge state of $Fe2^o$ will remain 4+ also after the introduction of the oxygen vacancies. In contrast, drastic changes occur in the chemical environment of $Fe1^s$ upon the conversion from octahedral to square-pyramidal coordination. Hence, it seems natural to expect a change in the oxidation state of $Fe1^s$ from 4+ to 3+ to maintain charge neutrality in the system. Moreover, as oxygen draws charge from neighboring atoms due to its larger electronegativity, it is natural to expect that a reduction in the number of coordinating oxygen ions would decrease the charge state of $Fe1^s$, viz. convert its oxidation state from 4+ to 3+. From this simple chemical picture, one can infer that the formal charge states of $Fe1^s$ and $Fe2^o$ in $Sr_4Fe_4O_{11}$ are 3+ and 4+, respectively. This observation is in agreement with Pauling's electrostatic valence rule,[7] which states that the electrostatic charges in an ionic crystal are locally balanced around every ion as evenly as possible.

Consistent with the above viewpoint, a search through Fe-, Co-, Ni-, and Cu-based oxides shows that, in oxides with mixed-valence ions, the lower oxidation-state ion quite generally prefers the site with the lower coordination number (CN) and vice versa. Examples involving Fe are Fe_3O_4 [Fe^{2+}(4); Fe^{3+}(6)] [where CN is given in parantheses, the valence assignments are based on data given in the ICSD databases,[8] whereas various other reports and elementary as well as advanced books record Fe_3O_4 as an inverse spinel (documented as an explanation for its anomalously high electrical conductivity;[9] see more details in Ref. 3) and $Na_9Fe_2O_7$ [Fe^{2+}(3); Fe^{3+}(4)],[10] for Co-based oxides Co_3O_4 [Co^{2+}(4); Co^{3+}(6)],[11] Co_2RuO_4 [Co^{2+}(4); Co^{3+}(6)],[12] $CoMn_2O_4$ [Co^{2+}(4); Co^{3+}(6)],[13] $Rb_5Co_2O_4$ [Co^{1+}(2); Co^{2+}(3)],[14] and $MnCo_2O_4$ [Co^{2+}(4); Co^{3+}(6)],[15] for Ni-based oxides $K_9Ni_2O_7$ [Ni^{2+}(3); Ni^{3+}(4)],[16] and for Cu-based oxides Cu_4O_3 [Cu^{1+}(2); Cu^{2+}(4)],[17] $TlCu_2O_2$ [Cu^{1+}(2); Cu^{2+}(4)],[18] $YBa_2Cu_3O_6$ [Cu^{1+}(2); Cu^{2+}(5)],[19] $LiCu_2O_2$ [Cu^{1+}(2); Cu^{2+}(5)],[20] $LiCu_3O_3$ [Cu^{1+}(2); Cu^{2+} (5 and 6)],[20] and $YPb_2Ba_2Cu_3O_8$ [Cu^{1+}(2); Cu^{2+}(5)].[21]

As Adler[2] relies on bond-length arguments, let us now analyze the validity of using the bond length to assign the oxidation state. The average Fe-O bond lengths ($d_{\text{Fe-O}}$) associated with $Fe1^s$ and $Fe2^o$ in $Sr_4Fe_4O_{11}$ are 1.864 and 2.008 Å, respectively. The $d_{\text{Fe-O}}$ for $Fe1O_5$ is shorter than that typical for Fe^{4+} ions (see Table 1 in Ref. 3), whereas $d_{\text{Fe-O}}$ for $Fe2O_6$ fits well with that for Fe^{3+}. However, for $Sr_3Fe_2O_6$ with Fe^{3+} in the square-pyramidal arrangement, the average $d_{\text{Fe-O}}$ is 1.961 Å (4×1.980 and 1×1.886 Å),[22] which is considerably larger than 1.864 Å. This has apparently misled Adler to believe that $Fe1^s$ of $Sr_4Fe_4O_{11}$ is in the 4+ state. As mentioned by Schmidt *et al.*,[5] no reference compound with Fe^{4+} in the square-pyramidal coordination with oxygen is available for comparison. The $d_{\text{Fe-O}}$ for square-pyramidal coordination in $Sr_4Fe_4O_{11}$ (1.864 Å) fits well with that for Fe^{3+} in tetrahedral (1.875 Å) coordination. On the contrary, the $Fe1^s$-O and $Fe2^o$-O bond lengths are longer than that for Fe^{4+} in tetrahedral and octahedral coordinations.

The actual oxidation state of an ion is decided by the charge residing on the ion. This information cannot be directly derived from experimental structure data. Moreover, $d_{\text{Fe-O}}$ depends not only on the oxidation state, but also on various other factors such as temperature, pressure, number and type of coordinating atoms, spin state of the ion concerned, etc. (A more detailed discussion on the influence of these parameters on $d_{\text{Fe-O}}$ is given in Ref. 3.) This is nicely demonstrated by the fact that for oxides with Fe^{3+} ions, $d_{\text{Fe-O}}$ varies between 1.875 and 2.125 Å depending on the CN (Table 1 in Ref. 3) and, consequently, $d_{\text{Fe-O}}$ alone cannot be used to deduce the charge state of Fe. The general conclusion is that no direct correlation can be established between $d_{\text{Fe-O}}$ and the oxidation state.

We have made additional analyses of chemical bonding [charge density, charge transfer, electron localization function (ELF), Born effective charges (BECs), partial density of states, and crystal orbital Hamilton population (COHP)] and derived Mössbauer parameters by *ab initio* calculations using the VASP (Ref. 23) and WIEN2K (Ref. 24) codes. (More details about the computational schemes are given in Ref. 3.) The present detailed reexamination of charge density, charge transfer, and ELF plots shows that the bonding interaction between Sr and O as well as between Fe and O have a dominant ionic character with non-negligible covalent components, viz. the chemical bonding in $Sr_4Fe_4O_{11}$ has a mixed ionocovalent character.

The BEC is a macroscopic concept,[25] which involves the polarization of the valence electrons as a whole, while the charge "belonging" to a given ion is an imprecisely defined concept. Ions with closed-shell-like character should (according to a rigid-ion picture) carry effective charges close to their nominal ionic value, whereas large amounts of nonrigid delocalized charge flow across the bonding skeleton during displacements of the ions of ionocovalent compounds.[26,27] Consequently, one will obtain effective charges much larger than the nominal ionic values in compounds with ionocovalent bonding. The calculated average diagonal components of the BEC for Sr, $Fe1^s$, $Fe2^o$, and O atoms are 2.53, 3.54, 5.86, and −3.03, respectively. The average BEC value is less than 4 for $Fe1^s$ and larger than 4 for $Fe2^o$, indicating a justification for assigning the formal valence states as 3+ and 4+, respectively.

The calculated total density of states (DOS) for the $Fe1^s$ and $Fe2^o$ sites is shown in Fig. 1. The DOS for the $Fe1^s$ site is higher than that for the $Fe2^o$ site throughout the entire valence band. The integrated DOS (i.e., the number of states) up to the Fermi level yields the total charge within each atomic sphere, and the higher number of occupied states at the $Fe1^s$ site (6.44) compared with that at the $Fe2^o$ site (5.67) provides additional evidence for ascribing formal Fe^{3+} and Fe^{4+} to $Fe1^s$ and $Fe2^o$, respectively.

The COHP is an indicator of the nature of bonding interaction,[28] and the integrated COHP (ICOHP) provides a measure of bond strength. The calculated ICOHP for the Fe1-O bond (1.23) is greater than that for the Fe2-O bond (1.03), indicating that electrons on Fe1 participate more in bonding interactions than in exchange interactions. This is one of the reasons why $Fe1^s$ has a lesser magnetic moment than $Fe2^o$, even though it has more electrons at its disposal.

Adler[2] evidently puts more trust on trends in Mössbauer parameters to assign valence states of ions than the other approaches we have reported earlier.[1] However, rather than continue an apparently unfruitful dispute on a semiqualitative basis, we decided to try to simulate Mössbauer parameters for $Sr_4Fe_4O_{11}$ and related oxides by first-principles calculations. The extraction of the Mössbauer parameters from experimental spectra for complex materials with crystallographically different sites is often difficult since the interconnection between the various effects is difficult to resolve and the overall picture is far from transparent. Therefore, reliable

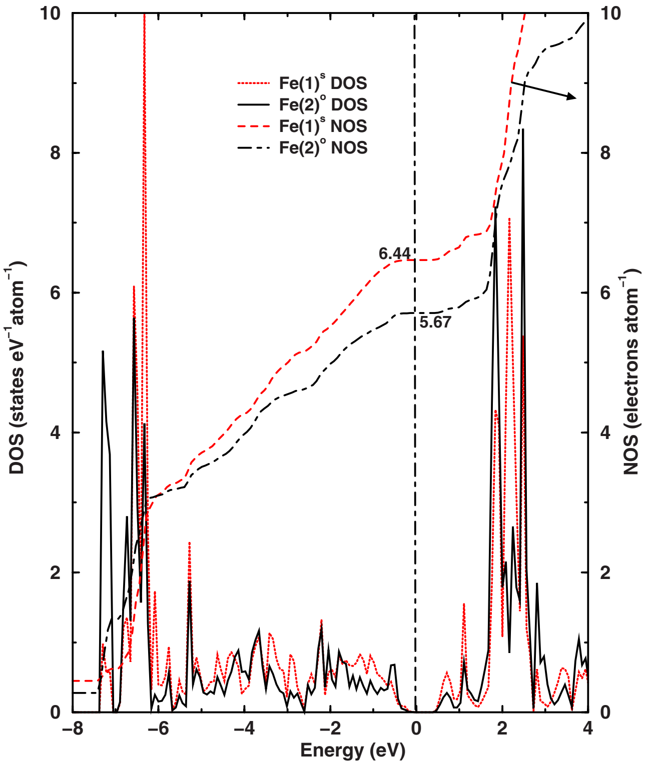

FIG. 1. (Color online) The calculated site-projected DOS and the number of states (NOS) at the Fe1^s and Fe2^o sites in $Sr_4Fe_4O_{11}$. The Fermi level is set to zero.

first-principles calculations are highly needed in order to provide a theoretical basis for the understanding of the experimentally established Mössbauer parameters. Owing to space limitations, here we only present a brief overview of the computationally derived hyperfine field (B_{HF}), isomer shift (Δ_{IS}), and quadrupole splitting (Δ_Q) parameters for $Sr_4Fe_4O_{11}$, whereas the full account for these findings is given in Ref. 3.

The hyperfine field is used as a local probe of magnetism based on the empirical fact that B_{HF} is, to a good approximation, proportional to the local magnetic moment. The magnetic moment at the two nonequivalent Fe sites (Fe1: $2.858\mu_B$ and Fe2: $3.531\mu_B$) in $Sr_4Fe_4O_{11}$ differ by $0.673\mu_B$, reflecting the differences in the local environment. This has important consequences for the distribution of the hyperfine field (HF) on different sites within the unit cell of $Sr_4Fe_4O_{11}$. Theoretical knowledge about different contributions to the B_{HF} is important to rationalize the development of the hyperfine field at different sites in mixed-valent systems. The B_{HF} is composed of four terms: contributions from core polarization (B_{Core}), valence (B_{Val}), orbital moment (B_{Orb}), and dipolar (B_{Dip}) fields. Among these, B_{Core} is found to be the deciding factor for B_{HF} at both Fe sites in $Sr_4Fe_4O_{11}$. [For Fe1^s and Fe^o, respectively (values in T), $B_{Core}=-35.825$ and -45.778, $B_{Val}=18.782$ and 16.262, $B_{Orb}=1.44$ and -1.86, and $B_{Dip}=5.55$ and -1.52, whereas lattice contributions to the B_{HF} are estimated to be of the order of 10^{-3} T.] The B_{Core} contribution is, indeed, directly related to the magnetic moment at the given Fe site.

TABLE I. Calculated Mössbauer parameters in $Sr_4Fe_4O_{11}$ and related oxides. Experimental values are given in brackets.

Compound	Atom	B_{HF} (T)	Δ_{IS} (mm s^{-1})	Δ_Q (mm s^{-1})
$Sr_4Fe_4O_{11}$	Fe1^s	−20.79	0.136 (−0.03)	0.146 (0.35)
	Fe2^o	−46.62 (45)	0.572 (0.47)	−0.434 (−0.67)
$SrFeO_3$	Fe^o	−35.77 (33)	0.291 (0.15)	0.135
$Sr_2Fe_2O_5$	Fe1^o	−28.05 (54)	0.649 (0.49)	0.411
	Fe2^t	−31.95 (45)	0.361 (0.29)	0.854
$Sr_3Fe_2O_6$	Fe^s	−23.61 (52)	0.522 (0.48)	0.315
$LaFeO_3$	Fe^o	−52.54 (56)	0.620 (0.47)	−0.052

The quantity that decides the charge state of an ion is the total charge at each site. The measured B_{HF}, on the other hand, reflects the spin density at a given site, which is the difference between the majority- and minority-spin electrons at the site concerned. As the spin density is independent of the total charge density but rather depends on the exchange interaction, one cannot obtain information about the valence states of Fe1^s and Fe2^o from the measured HF of Fe in $Sr_4Fe_4O_{11}$.

The isomer shift is determined by the *s* electron density at the nucleus, which depends on the degree of localization of the electrons at a particular site (i.e., localized electrons have large contact density and, correspondingly, large Δ_{IS}). It is often problematic to assign the experimentally observed Δ_{IS} for a given atomic site in mixed-valent systems.[29]

Calculated Δ_{IS} values are given in Table I. Changes in the shape of *s*-electron distribution by shielding and hybridization effects are the main reasons for the difference in Δ_{IS} between the different Fe ions in $Sr_4Fe_4O_{11}$. Based on our band-structure results (see above and Refs. 1 and 3), we formally assigned Fe1^s as Fe^{3+}. The presence of covalence in the Fe1^s-O bonds reduces the charge density at the Fe nucleus and, hence, Δ_{IS} becomes lower than usually expected for an Fe^{3+} ion. The actual size of Δ_{IS} is not only determined by the charge state, but also by coordination number, bond length, spin state, nature of bonding interaction with neighbors, etc. On the other hand, the charge state of an Fe ion is decided by the valence electrons that comprise of not only *s*, but also *p* and *d* electrons. From a detailed analysis of the origin of the isomer shift,[3] it is clear that one cannot obtain information about the total charge density at the probe site (the deciding factor for the valence state). So, Δ_{IS} measured for pure ionic compounds cannot be taken as references for assigning the oxidation state for constituents in compounds with partial covalence. In brief, it can be said that the magnitude of the Δ_{IS} at the two different Fe sites in $Sr_4Fe_4O_{11}$ rather reflects the strength of the covalent bonding between them and oxygen, than their charge state.

The quadrupole splitting may provide a rather indirect indication of the charge state, but it is usually impossible to draw unambiguous conclusions regarding the charge distribution from Δ_Q.[30] However, we have been able to reproduce the experimentally reported Δ_Q for the Fe1^s and Fe2^o sites in

$Sr_4Fe_4O_{11}$ (see Table I). The oxygen vacancies play an important role in determining the distribution of the charge density at the $Fe1^s$ site and, in particular, the redistribution of the electron density around the $Fe1^s$ nucleus (in a manner that changes Δ_Q from negative to positive). A more detailed analysis shows that Δ_Q does not depend on the total charge at each site, but rather depends on the anisotropy in the charge distribution at the nucleus. Note that for an Fe^{3+} ion in a given structural framework, Δ_Q increases with increasing distortion of the coordination polyhedron.[31] Even if two sites have the same total charge, the anisotropy in the charge distribution will be different and, hence, Δ_Q will be different. Thus, Δ_Q is determined by the site symmetry of the atom, the character of the electrons involved in the bonding interaction with the neighbors, coordination number, interatomic distance, etc. Therefore, the value of Δ_Q obtained from experimental Mössbauer data is not appropriate to unambiguously assign the oxidation state of ions.

The brief conclusion is that all evidences that we have been able to collect point at Fe^{3+} and Fe^{4+} as the correct assignments of formal oxidation states for the $Fe1^s$ and $Fe2^o$ sites, respectively, in $Sr_4Fe_4O_{11}$. For a detailed description of various arguments used to arrive at the present conclusion, readers are referred to Ref. 3.

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