Reply to “Comment on ‘Spin- and charge-ordering in oxygen-vacancy-ordered mixed-valence \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \)’”

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Recently, using density-functional theoretical calculations, we have reported [Phys. Rev. B 74, 054422 (2006)] that formal \( \text{Fe}^{3+} \) ions reside at the square-pyramidal site and \( \text{Fe}^{4+} \) ions at the octahedral site in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). 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 \( \text{Fe} \) in the square-pyramidal and octahedral environments in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). From a critical examination of the structure data for \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) and related oxides with \( \text{Fe} \) 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 \( \text{Fe}^{3+} \) and \( \text{Fe}^{4+} \) to the square-pyramidal and octahedral sites, respectively, in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \).

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Recently, using density-functional theoretical calculations, we have reported that formal \( \text{Fe}^{3+} \) ions reside at the square-pyramidal sites and \( \text{Fe}^{4+} \) ions at the octahedral sites in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). Based on the interpretation of experimental structure and Mössbauer data from the literature, Adler concludes that our previous first-principles results disagree with the experimental findings with regard to the assignment of oxidation states to \( \text{Fe} \) in the \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). 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 \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) and, thus, strengthen our conclusions. Owing to space limitations, more detailed analyses and discussions are provided in a subsequent paper.

The crystal structure of \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) comprises two nonequivalent iron atoms in equal amounts (\( \text{Fe}^1 \) in square-pyramidal and \( \text{Fe}^2 \) 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 \( \text{Fe}^1 \) and \( \text{Fe}^2 \) sites are occupied by (formally) \( \text{Fe}^{3+} \) and \( \text{Fe}^{4+} \), respectively, with AF ordering of the \( \text{Fe}^2 \) moments. We would like to specifically emphasize that this conclusion does not contradict the experimental results of Hodges et al. and Schmidt et al., but rather the interpretation of the experiments with regard to the assignment of oxidation state for the two different \( \text{Fe} \) ions in Ref. 4 and the specification of which of the \( \text{Fe} \) ions exhibits long-range magnetic ordering in Ref. 5.

Hodges et al. used a bond-strength model proposed by Ziolkowski to assign the \( 4+ \) and \( 3+ \) oxidation states to the \( \text{Fe}^1 \) and \( \text{Fe}^2 \) 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 \( z \). Therefore, for a complex oxide such as \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \), individual bond-strength sums for crystallographically nonequivalent \( \text{Fe} \) ions may not be meaningful. So, Schmidt et. al. compared the bond-strength sums over all \( \text{Fe} \) sites of the unit cell derived using two different models; one with \( \text{Fe}^{3+} \) at \( \text{Fe}^1 \) and \( \text{Fe}^{4+} \) at \( \text{Fe}^2 \) 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 \( \text{Fe}^1 \) and \( \text{Fe}^2 \) sites based on bond-strength considerations. Hence, Schmidt et al. used chemical insight and crystal structure information for \( \text{Sr}-\text{Fe}-\text{O} \) 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 \( \text{Fe} \) would evolve upon the introduction of oxygen vacancies into the pristine \( \text{SrFeO}_3 \) lattice. It is generally accepted that \( \text{Fe} \) donates electrons and \( \text{O} \) accepts electrons in a \( \text{Sr}-\text{Fe}-\text{O} \) lattice. According to an ideal ionic picture and a fully oxygen-ordered system, \( \text{Fe} \) is surrounded by six oxygens in the \( 2- \) state. As \( \text{Sr} \) formally prefers the \( 2+ \) state, one can ascribe a formal charge of \( 4+ \) to all \( \text{Fe} \) ions in \( \text{SrFeO}_3 \). On the other hand, if one systematically removes one apical oxygen from alternate \( \text{FeO}_6 \) structural subunits of \( \text{SrFeO}_3 \), one obtains \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) with an equal number of \( \text{Fe} \) in square-pyramidal (\( \text{Fe}^{3+} \)) and octahedral (\( \text{Fe}^{4+} \)) coordinations. As the local environment of the octahedra will be approximately the same as that in \( \text{SrFeO}_3 \), one would expect that the formal charge state of \( \text{Fe}^{2+} \) will remain \( 4+ \) also after the introduction of the oxygen vacancies. In contrast, drastic changes occur in the chemical environment of \( \text{Fe}^1 \) upon the conversion from octahedral to square-pyramidal coordination. Hence, it seems natural to expect a change in the oxidation state of \( \text{Fe}^1 \) 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 Fe$^{3+}$, viz. convert its oxidation state from 4+ to 3+. From this simple chemical picture, one can infer that the formal charge states of Fe$^{4+}$ and Fe$^{2+}$ in Sr$_4$Fe$_4$O$_{11}$ are 3+ and 4+, respectively. This observation is in agreement with Pauling’s electrostatic valence rule, 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$_2$O$_3$ [$Fe^{2+}(4)$; Fe$^{3+}(6)$] [where CN is given in parentheses, the valence assignments are based on data given in the ICD databases, whereas various other reports and elementary as well as advanced books record Fe$_2$O$_3$ as an inverse spinel (documented as an explanation for its anomalously high electrical conductivity]; see also more details in Ref. 3] and Na$_2$Fe$_2$O$_4$ [$Fe^{2+}(3)$; Fe$^{3+}(4)$] for Co-based oxides Co$_2$O$_4$ [$Co^{2+}(4)$; Co$^{3+}(6)$]; Co$_2$RuO$_4$ [$Co^{2+}(4)$; Co$^{3+}(6)$]; Co$_2$Mo$_2$O$_4$ [$Co^{2+}(4)$; Co$^{3+}(6)$]; Rh$_2$Co$_2$O$_4$ [$Co^{2+}(2)$; Co$^{3+}(5)$]; and Mn$_2$Co$_2$O$_4$ [$Co^{2+}(4)$; Co$^{3+}(6)$]. For Ni-based oxides K$_2$Ni$_2$O$_7$ [$Ni^{2+}(3)$; Ni$^{3+}(4)$] and for Cu-based oxides Cu$_2$O$_3$ [$Cu^{+}(2)$; Cu$^{2+}(4)$]; TICu$_2$O$_4$ [$Cu^{+}(2)$; Cu$^{2+}(5)$]; LiCu$_2$O$_4$ [$Cu^{+}(2)$; Cu$^{2+}(5)$]; YBC$_2$Cu$_4$O$_8$ [$Cu^{+}(2)$; Cu$^{2+}(5)$]; LiCu$_2$O$_4$ [$Cu^{+}(2)$; Cu$^{2+}(5)$]; LiCu$_2$O$_4$ [$Cu^{+}(2)$; Cu$^{2+}(5)$]; and YPB$_2$Ba$_2$Cu$_4$O$_8$ [$Cu^{+}(2)$; Cu$^{2+}(5)$].

As Adler 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 ($d_{Fe-O}$) associated with Fe$^{3+}$ and Fe$^{2+}$ in Sr$_4$Fe$_4$O$_{11}$ are 1.864 and 2.008 Å, respectively. The $d_{Fe-O}$ for Fe$^{2+}$ is shorter than that typical for Fe$^{3+}$ ions (see Table 1 in Ref. 3), whereas $d_{Fe-O}$ for Fe$^{2+}$ fits well with that for Fe$^{3+}$. However, for Sr$_4$Fe$_2$O$_4$, with Fe$^{3+}$ in the square-pyramidal arrangement, the average $d_{Fe-O}$ is 1.961 Å ($4 \times 1.980$ and $1 \times 1.886$ Å), which is considerably larger than 1.864 Å. This has apparently misled Adler to believe that Fe$^{3+}$ of Sr$_4$Fe$_2$O$_{11}$ is in the 4+ state. As mentioned by Schmidt et al., no reference compound with Fe$^{3+}$ in the square-pyramidal coordination with oxygen is available for comparison. The $d_{Fe-O}$ for square-pyramidal coordination in Sr$_4$Fe$_2$O$_{11}$ (1.864 Å) fits well with that for Fe$^{3+}$ in tetrahedral (1.875 Å) coordination. On the contrary, the Fe$^{3+}$-O and Fe$^{2+}$-O bond lengths are longer than that for Fe$^{3+}$ 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, $d_{Fe-O}$ 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 $d_{Fe-O}$ is given in Ref. 3.) This is nicely demonstrated by the fact that for oxides with Fe$^{3+}$ ions, $d_{Fe-O}$ varies between 1.875 and 2.125 Å depending on the CN (Table 1 in Ref. 3) and, consequently, $d_{Fe-O}$ alone cannot be used to deduce the charge state of Fe. The general conclusion is that no direct correlation can be established between $d_{Fe-O}$ 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$_4$Fe$_4$O$_{11}$ has a mixed ionic-covalent character.

The BEC is a macroscopic concept, 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 in ionic-covalent compounds. Consequently, one will obtain effective charges much larger than the nominal ionic values in compounds with ionic-covalent bonding. The calculated average diagonal components of the BEC for Sr, Fe$^{3+}$, Fe$^{2+}$, and O atoms are 2.53, 3.54, 5.86, and −3.03, respectively. The average BEC value is less than 4 for Fe$^{3+}$ and larger than 4 for Fe$^{2+}$, indicating a justification for assigning the formal valence states as 3+ and 4+, respectively.

The calculated total density of states (DOS) for the Fe$^{3+}$ and Fe$^{2+}$ sites is shown in Fig. 1. The DOS for the Fe$^{3+}$ site is higher than that for the Fe$^{2+}$ 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 Fe$^{3+}$ site (6.44 compared with that at the Fe$^{2+}$ site (5.67) provides additional evidence for ascribing formal Fe$^{3+}$ and Fe$^{2+}$ to Fe$^{3+}$ and Fe$^{2+}$, respectively.

The COHP is an indicator of the nature of bonding interaction, and the integrated COHP (ICOHP) provides a measure of bond strength. The calculated ICOHP for the Fe$^{3+}$-O bond (1.23) is greater than that for the Fe$^{2+}$-O bond (1.03), indicating that electrons on Fe participate more in bonding interactions than in exchange interactions. This is one of the reasons why Fe$^{3+}$ has a lesser magnetic moment than Fe$^{2+}$, even though it has more electrons at its disposal.

Adler evidently puts more trust on trends in Mössbauer parameters to assign valence states of ions than the other approaches we have reported earlier. However, rather than continue an apparently unfruitful dispute on a semiquantitative basis, we decided to try to simulate Mössbauer parameters for Sr$_4$Fe$_2$O$_{11}$ 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
Theoretical knowledge about different contributions to the field important consequences for the distribution of the hyperfine and \( B_{HF} \) fields. Among these, \( B_{HF} \) 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 \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). [For Fe\( 1^s \) and Fe\( 2^o \), 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.

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 (\( \Delta IS \)), and quadrupole splitting (\( \Delta Q \)) parameters for \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \), 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 (Fe\( 1^s \) and Fe\( 2^o \)) in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) differ by \( \mu_B \), 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 \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). 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 \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). [For Fe\( 1^s \) and Fe\( 2^o \), 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.

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 \( \Delta IS \)). It is often problematic to assign the experimentally observed \( \Delta IS \) for a given atomic site in mixed-valent systems.

Calculated \( \Delta IS \) 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 \( \Delta IS \) between the different Fe ions in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \). Based on our band-structure results (see above and Refs. 1 and 3), we formally assigned Fe\( 1^s \) as Fe\( 3^+ \). The presence of covalence in the Fe\( 1^s \)-O bonds reduces the charge density at the Fe nucleus and, hence, \( \Delta IS \) becomes lower than usually expected for an Fe\( 3^+ \) ion. The actual size of \( \Delta IS \) 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, 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, \( \Delta IS \) 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 \( \Delta IS \) at the two different Fe sites in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) 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 \( \Delta Q \). However, we have been able to reproduce the experimentally reported \( \Delta Q \) for the Fe\( 1^s \) and Fe\( 2^o \) sites in

### Table I. Calculated Mössbauer parameters in \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) and related oxides. Experimental values are given in brackets.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>( B_{HF} ) (T)</th>
<th>( \Delta IS ) (mm s(^{-1} ))</th>
<th>( \Delta Q ) (mm s(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sr}_4\text{Fe}<em>4\text{O}</em>{11} )</td>
<td>Fe( 1^s )</td>
<td>−20.79</td>
<td>0.136 (−0.03)</td>
<td>0.146 (0.35)</td>
</tr>
<tr>
<td></td>
<td>Fe( 2^o )</td>
<td>−46.62 (45)</td>
<td>0.572 (0.47)</td>
<td>−0.434 (−0.67)</td>
</tr>
<tr>
<td>( \text{SrFeO}_3 )</td>
<td>Fe( o )</td>
<td>−35.77 (33)</td>
<td>0.291 (0.15)</td>
<td>0.135</td>
</tr>
<tr>
<td>( \text{Sr}_2\text{Fe}_2\text{O}_5 )</td>
<td>Fe( 1^o )</td>
<td>−28.05 (54)</td>
<td>0.649 (0.49)</td>
<td>0.411</td>
</tr>
<tr>
<td></td>
<td>Fe( 2^o )</td>
<td>−31.95 (45)</td>
<td>0.361 (0.29)</td>
<td>0.854</td>
</tr>
<tr>
<td>( \text{Sr}_3\text{Fe}_2\text{O}_6 )</td>
<td>Fe( o )</td>
<td>−23.61 (52)</td>
<td>0.522 (0.48)</td>
<td>0.315</td>
</tr>
<tr>
<td>( \text{LaFeO}_3 )</td>
<td>Fe( o )</td>
<td>−52.54 (56)</td>
<td>0.620 (0.47)</td>
<td>−0.052</td>
</tr>
</tbody>
</table>
Sr$_2$Fe$_4$O$_{11}$ (see Table I). The oxygen vacancies play an important role in determining the distribution of the charge density at the Fe$^{1+}$ site and, in particular, the redistribution of the electron density around the Fe$^{1+}$ nucleus (in a manner that changes \( \Delta_Q \) from negative to positive). A more detailed analysis shows that \( \Delta_Q \) 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, \( \Delta_Q \) 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, \( \Delta_Q \) will be different.

Thus, \( \Delta_Q \) 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 \( \Delta_Q \) 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 Fe$^{1+}$ and Fe$^{2+}$ sites, respectively, in Sr$_2$Fe$_4$O$_{11}$. For a detailed description of various arguments used to arrive at the present conclusion, readers are referred to Ref. 3.