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

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In a recent paper, Vidya *et al.* [Phys. Rev. B **74**, 054422 (2006)] investigated the structural, electronic, and magnetic properties of mixed-valence $Sr_4Fe_4O_{11}$ by spin-polarized electronic-structure calculations. The crystal structure of this oxygen-vacancy-ordered perovskite contains square pyramidal $Fe(1)^s$ and distorted octahedral $Fe(2)^o$ sites. Only one of the sublattices is magnetically ordered below $T_N \sim 230$ K. Vidya *et al.* claimed that their calculations unambiguously show that the formal Fe^{3+} ions reside in the square pyramidal and the Fe^{4+} ions in the octahedral sites, in contrast to the previous assignment by Hodges *et al.* [J. Solid State Chem. **151**, 190 (2000)]. In addition, Vidya *et al.* implied that rather the Fe^{4+} than the Fe^{3+} sublattice is magnetically ordered. In this Comment, it is pointed out that the structural and Mössbauer data clearly favor the assignment of Hodges *et al.* and are in disagreement with the results of Vidya *et al.* The Mössbauer spectra evidence that it is the Fe^{3+} sublattice which is magnetically ordered.

The oxygen-deficient perovskite-type ferrate $Sr_4Fe_4O_{11}$ ($SrFeO_{2.75}$) with formally 50% Fe^{4+} and 50% Fe^{3+} ions has found interest due to its peculiar electronic and magnetic properties.[1–5] It is generally accepted that the crystal structure of $Sr_4Fe_4O_{11}$ reveals two crystallographically distinct sites $Fe(1)^s$ and $Fe(2)^o$, where $Fe(1)^s$ and $Fe(2)^o$ are square pyramidal and distorted octahedral sites, respectively.[6] Most remarkably, the Mössbauer spectra[1–4] and powder neutron diffraction studies[5] have shown that only one of the sublattices is magnetically ordered below $T_N \sim 230$ K, whereas the other remains disordered down to 4 K. In order to derive the magnetic structure, it is of crucial importance to relate correctly the iron charge states with the respective crystallographic sites. This issue has led, however, to considerable controversy. Whereas Hodges *et al.*[6] concluded from bond-valence sum calculations that the Fe^{4+} sites reside in the $Fe(1)O_5$ and the Fe^{3+} sites in the $Fe(2)O_6$ units, Schmidt *et al.*[5] criticized this assignment and favored the opposite distribution of charge states. In a recent work, Vidya *et al.* investigated the structural, electronic, and magnetic properties of $Sr_4Fe_4O_{11}$ by spin-polarized electronic-structure calculations and claimed that their "theoretical results show unambiguously that Fe atoms with the square pyramidal environment have a lower oxidation state than that in the octahedral coordination"[7] which would support the suggestion of Schmidt *et al.* Furthermore, Vidya *et al.* challenged the conventional interpretation of the Mössbauer spectra[1–4] and suggested that the magnetic hyperfine sextet seen at low temperature rather corresponds to magnetically ordered Fe^{4+} than Fe^{3+} sites. In this Comment, we reconsider the structural and Mössbauer data of $Sr_4Fe_4O_{11}$ and emphasize that they clearly favor the assignment by Hodges *et al.*, but are in disagreement with the theoretical calculations of Vidya *et al.* Accordingly, the discussion of the magnetic structure presented in Ref. 7, which is based on the incorrect charge assignment, is misleading.

We have already pointed out recently[8] that the correct charge assignments for $Sr_4Fe_4O_{11}$ can be derived by considering the bond distances and comparing them with related compounds. The average Fe-O distance d_{Fe-O} for the $Fe(2)^o$ sites is 2.01 Å (4×2.044 Å, 2×1.937 Å), which compares

well with d_{Fe-O} in related Fe^{3+} oxides [for instance, d_{Fe-O} =2.01 Å in $LaFeO_3$ (Ref. 9) and $SrLaFeO_4$ (Ref. 10)]. On the other hand, d_{Fe-O} is considerably smaller in Fe^{4+} oxides (for instance, d_{Fe-O}=1.93 Å and d_{Fe-O}=1.94 Å in $SrFeO_3$ (Ref. 6) and Sr_2FeO_4,[11] respectively). The strong structural distortion of the $Fe(2)O_6$ octahedra does not contradict an assignment to Fe^{3+} as structurally distorted Fe^{3+} sites are not uncommon in perovskite-related ferrates [cf. the crystal structures of $SrLaFeO_4$ (Ref. 10) and $Sr_2Fe_2O_5$ (Ref. 12)]. Therefore, the compressed $Fe(2)O_6$ units are not in favor of a Jahn–Teller effect of Fe^{4+}. In this case, one rather would expect an elongated octahedron, as has been indeed found in K_2NiF_4-related phases with nearly isolated $Fe^{4+}O_6$ units.[13,14] As the number of pure Fe^{4+} oxides is quite limited, there is indeed no reference compound with square pyramidal FeO_5 units in this oxidation state as has been noticed by Schmidt *et al.*[5] Nevertheless, d_{Fe-O}=1.86 Å for the $Fe(1)O_5$ units in $Sr_4Fe_4O_{11}$ is much smaller than d_{Fe-O}=1.97 Å in case of the Fe^{3+} oxide $Sr_3Fe_2O_6$,[15] the crystal structure of which contains FeO_5 square pyramids. Accordingly, relating $Fe(1)^s$ to Fe^{4+} and $Fe(2)^o$ to Fe^{3+} as derived by Hodges *et al.*[6] leads to the expected trends in bond distances, whereas the opposite assignment favored by Schmidt *et al.*[5] and Vidya *et al.*[7] would lead to unreasonably long Fe^{4+}-O and short Fe^{3+}-O distances, respectively. It is noted that the overall bonding pattern derived from the theoretical calculations in Ref. 7 with more covalent Fe1-O than Fe2-O bonding is rather in agreement with our charge assignment as Fe^{4+}-O bonding generally is more covalent than Fe^{3+}-O bonding. The strongly covalent Fe^{4+}-O bonding is at the origin of the interesting physics of Fe^{4+} oxides which are frequently classified as negative-charge-transfer energy (negative-Δ) materials.[16] Square pyramidal FeO_5 units with very similar bond distances as in $Sr_4Fe_4O_{11}$ are also observed in the crystal structure of $Sr_8Fe_8O_{23}$.[6] A consistent description of sample composition, structural data, and the Mössbauer spectra of this oxide is only achieved if the FeO_5 units are associated with Fe^{4+} ions.[6,8]

We now turn to the Mössbauer parameters of $Sr_4Fe_4O_{11}$, which are summarized in Table I, and for comparison data of related oxides, which are given in Table II. In their paper,

TABLE I. Mössbauer parameters (IS: isomer shift vs α-Fe; B_{hf}: hyperfine field; ε: quadrupole interaction parameter; ΔE_Q: quadrupole splitting) of $Sr_4Fe_4O_{11}$ from Ref. 8. Similar values were reported in Ref. 2.

T (K)	Assignment	IS (mm s^{-1})	ε or ΔE_Q (mm s^{-1})	B_{hf} (T)
4	Fe^{4+}	−0.03	0.35	
	Fe^{3+}	0.47	−0.67	45
295	Fe^{4+}	−0.09	0.32	
	Fe^{3+}	0.34	1.35	

TABLE II. Mössbauer ISs vs α-Fe and hyperfine fields B_{hf} for some Fe^{3+} and Fe^{4+} oxides at 4 K (o, s, and t refer to octahedral, square pyramidal, and tetrahedral coordination, respectively).

Compound	Fe charge state	IS (mm s^{-1})	B_{hf} (T)	Ref.
$LaFeO_3$	$+3^o$	0.47	56	9
$Sr_2Fe_2O_5$	$+3^o$	0.49	54	17
	$+3^t$	0.29	45	
$Sr_3Fe_2O_6$	$+3^s$	0.48	52	18
$SrFeO_3$	$+4^o$	0.15	33	17
Sr_2FeO_4	$+4^o$	0.07	25–33	11
$SrLaMg_{0.5}Fe_{0.5}O_4$	$+4^o$	−0.09	18	14

Vidya *et al.* considered charge assignments based on the Mössbauer isomer shifts (ISs) as ambiguous as the reference standards are not "real standards in the sense that they provide a fixed valence state of Fe."[7] In fact, relying on absolute values of IS (and B_{hf}) may be misleading, but comparison of the trends in related compounds allows definite clues to be drawn and is a well accepted procedure. In case of $Sr_4Fe_4O_{11}$, there is no ambiguity in the assignment of charge states from the Mössbauer isomer shifts. Referring to the 4 K spectrum of $Sr_4Fe_4O_{11}$ (Ref. 8) (or to the 77 K spectrum from Ref. 2), it is evident that the magnetically ordered site with $B_{hf} \sim 45$ T is characterized by IS=0.47 mm s^{-1}. This IS value is typical for Fe^{3+} in such oxides (see Table II) and safely rules out an assignment to Fe^{4+}. Therefore, the hyperfine pattern at low temperatures is clearly associated with the Fe^{3+} and not with the Fe^{4+} sites as has been implied in Ref. 7. The Fe^{3+} sites are subjected to a large quadrupole interaction in the paramagnetic as well as in the magnetically ordered phase which is in agreement with the pronounced structural distortion of the $Fe(2)O_6$ units. On the other hand, the quadrupole doublet with IS=−0.03 mm s^{-1} and a smaller quadrupole splitting suggest electronically rather localized Fe^{4+} ions located in the $Fe(1)^s$ sites, which remain magnetically disordered down to 4 K. The calculations of Ref. 7 confirm that the absolute value of the electric field gradient is much larger at the $Fe(2)^o$ than at the $Fe(1)^s$ sites. Neglecting differences in the $4s$ contributions to the chemical bonding between the two coordination environments, it is concluded that the number of d electrons, which shield the s-electron density from the nucleus, is smaller for the $Fe^{4+}(1)^s$ than for the $Fe^{3+}(2)^o$ sites, again in disagreement with the results of Ref. 7.

Combing the information from the structural and Mössbauer data, it is deduced that a G-type antiferromagnetic spin arrangement occurs, which is driven by the strong antiferromagnetic interactions between the half-filled $t_{2g}^3 e_g^2$ shells of the Fe^{3+} sites in the vertex-sharing $Fe(2)O_6$ chains. The coupling between the chains is much weaker. As suggested by Gibb[2] and Hodges *et al.*[6] the $Fe^{4+}(1)^s$ spins are subjected to competing magnetic interactions. This leads to rapid spin fluctuations and prevents development of long-range magnetic order of the $Fe(1)^s$ sublattice. Quantum fluctuations even at low temperature in this peculiar magnetic structure with strong antiferromagnetic interactions only in one dimension are the likely origin for the quite small $B_{hf}=45$ T, which is, however, still much higher than any known B_{hf} value for Fe^{4+} oxides.

In summary, the available structural and Mössbauer data evidence that the $Fe(1)^s$ and $Fe(2)^o$ sites in the crystal structure of $Sr_4Fe_4O_{11}$ correspond to Fe^{4+} and Fe^{3+} ions, respectively. The $Fe^{3+}(2)^o$ sublattice is antiferromagnetically ordered, whereas the $Fe^{4+}(1)^s$ sublattice remains disordered. Accordingly, not the experimentalists have been "mislead to believe that magnetic ordering occurs for Fe^{3+} rather than for Fe^{4+}"[7] but the theoretical calculations presented in Ref. 7 are not in accord with the experimental observations.

[1] T. C. Gibb, J. Chem. Soc. Dalton Trans. **1985**, 1455 (1985).

[2] T. C. Gibb, J. Mater. Chem. **4**, 1445 (1994).

[3] Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama, and Y. Bando, J. Solid State Chem. **63**, 237 (1986).

[4] M. Takano, T. Okita, N. Nakayama, Y. Bando, Y. Takeda, O. Yamamoto, and J. B. Goodenough, J. Solid State Chem. **73**, 140 (1988).

[5] M. Schmidt, M. Hofmann, and S. J. Campbell, J. Phys.: Condens. Matter **15**, 8691 (2003).

[6] J. P. Hodges, S. Short, J. D. Jorgensen, X. Xiong, B. Dabrowski, S. M. Mini, and C. W. Kimball, J. Solid State Chem. **151**, 190 (2000).

[7] R. Vidya, P. Ravindran, H. Fjellvåg, and A. Kjekshus, Phys. Rev. B **74**, 054422 (2006).

[8] P. Adler, A. Lebon, V. Damljanović, C. Ulrich, C. Bernhard, A. V. Boris, A. Maljuk, C. T. Lin, and B. Keimer, Phys. Rev. B **73**, 094451 (2006).

[9] S. E. Dann, D. B. Currie, M. T. Weller, M. F. Thomas, and A. D. Al-Rawwas, J. Solid State Chem. **109**, 134 (1994).

[10] J. L. Soubeyroux, P. Courbin, L. Fournes, D. Fruchart, and G. le Flem, J. Solid State Chem. **31**, 313 (1980).

[11] S. E. Dann, M. T. Weller, D. B. Currie, M. F. Thomas, and A. D.

Al-Rawwas, J. Mater. Chem. **3**, 1231 (1993).

[12] M. Harder and H. Müller-Buschbaum, Z. Anorg. Allg. Chem. **464**, 169 (1980).

[13] J. L. Soubeyroux, N. Chevreau, G. Demazeau, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **51**, 38 (1984).

[14] G. Demazeau, Z. Li-Ming, L. Fournes, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **72**, 31 (1988).

[15] S. E. Dann, M. T. Weller, and D. B. Currie, J. Solid State Chem. **97**, 179 (1992).

[16] A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda, and M. Takano, Phys. Rev. B **45**, 1561 (1992).

[17] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, J. Chem. Phys. **41**, 2429 (1964).

[18] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, J. Chem. Phys. **45**, 2466 (1966).