Layered Oxides

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Square-Planar Coordinated Iron in the Layered Oxoferrate(II) $SrFeO_2$

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iron · magnetism · oxygen · solid-state structures · $SrFeO_2$

Iron, one of the most abundant elements in the earth's crust, forms numerous oxides,[1] some of which are widely used in industry as low-cost ferrite magnets and pigments. They show a wide variety of electronic properties, ranging from insulating to metallic behavior. Also their magnetic properties, where everything is found from Pauli paramagnetism to local magnetic moment behavior including the occurrence of ferromagnetism and antiferromagnetism, are of great diversity. Among complex iron oxides, $SrFeO_{3-x}$ $(0<x<0.5)$ and its related iron perovskite oxides exhibit fast oxygen transport and high electron conductivity even at low temperatures, so they are ideal materials for applications such as giant magnetoresistance materials,[2] electrodes for membranes in oxygen separation,[3] solid-state gas sensors,[4] solid oxide fuel cells and batteries,[5] and catalysts.[6]

Until recently, the most reduced phase known within the Sr–Fe–O system was the oxoferrate(III) $SrFeO_{2.5}$ $(x=0.5)$, the so-called brownmillerite.[7] A few months ago, Tsujimoto et al.[8] reported on the synthesis of the first ternary earth alkaline oxoferrate(II), $SrFeO_2$, by the reduction of an easy-to-prepare, slightly oxygen-deficient perovskite $SrFeO_{3-x}$ precursor $(x\approx 0.125)$ at low temperatures (ca. 400 K) with CaH_2. The residual CaH_2 and the CaO byproduct were washed out with an NH_4Cl/methanol solution. The key for the preparation of this oxide was the use of a hydride of an electropositive metal (CaH_2) as powerful reducing agent, which is active at considerably lower temperatures than when conventional techniques are used. In the last decade, this method has been successfully applied for the syntheses of several oxides containing 3d transition elements in unusual low oxidation states, for example, $LaSrCoO_{3.38}$,[9] $YSr_2Mn_2O_{5.5}$,[10] and $La_3Ni_2O_6$[11].

The tetragonal structure of $SrFeO_2$ ($P4/mmm$, $a=399.11$ and $c=347.48$ pm) is isotypic with $SrCuO_2$.[12] $SrFeO_2$ contains checkerboard-like layers of corner-sharing FeO_4 squares with strontium atoms in between, (Figure 1 a), and closely resembles the sheet-like lattice geometry of superconducting copper oxides.[13] The Fe–O distances of 199.5 pm are as expected for four-coordinated iron(II). At first glance however, it appears unusual for iron(II) with d^6 configuration to have a square-planar coordination of oxygen atoms, as it is well known that in oxides, iron(II) has octahedral, tetrahedral, or, rarely, planar coordination with three oxygen atoms, as in Na_4FeO_3.[14] Only in the mineral gillespite, $BaFeSi_4O_{10}$,[15] is square-planar coordination of oxygen around iron to be found. In this case, however, the FeO_4 squares are not condensed with each other. A similar situation of a square-planar-coordinated transition metal atom with d^6 configuration is also found in the manganese(I) nitride Ce_2MnN_3, which contains chains of condensed planar MnN_4 units.[16]

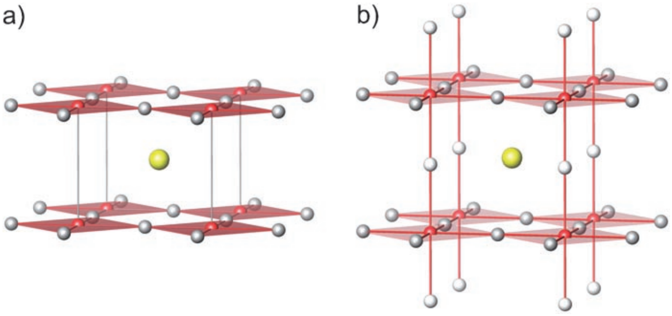

Figure 1. Perspective view of the crystal structures of a) the infinite-layer compound $SrFeO_2$ and b) the perovskite compound $SrFeO_3$. Fe red, Sr yellow, O gray spheres.

Doubts about the composition of $SrFeO_2$ can be resolved for several reasons. The incorporation of calcium can be excluded by analyses. The crystal structure of $SrFeO_2$ was obtained by Rietveld refinements from both synchrotron and neutron powder diffraction data. According to these refinements, the occupation of the oxygen position is unity within the standard deviation, and no extra oxygen atoms into the apical site between two iron atoms of neighboring layers were detected. The incorporation of hydrogen in the structure with the formation of an oxide hydride, as occurs when reducing $LaSrCoO_4$ with a hydride to $LaSrCoO_3H_{0.7}$,[17] could be excluded from the refinement of the neutron powder diffraction data. Furthermore, the calculated Madelung part of the lattice energy (MAPLE)[18] for $SrFeO_2$ is 1967.6 kcal mol^{-1} and deviates only by 0.4 % from the sum of the MAPLE values for the binary components SrO (902.5 kcal mol^{-1}) and FeO[19] (1072.3 kcal mol^{-1}). The small difference reflects the correct composition and the good structure refinement of $SrFeO_2$.

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The reduction of the oxygen-deficient perovskite $SrFeO_{3-x}$ ($x = 0.125$) to the new infinite-layer iron oxide $SrFeO_2$ can be considered as a kind of a topotactic synthesis, as the $FeO_{4/2}$ layers are already preformed in the precursor material (Figure 1b). If $SrFeO_2$ is heated gently under oxygen, it readily oxidizes back to the perovskite $SrFeO_{3-x}$, demonstrating that oxide ions can be reinserted into the lattice quite easily. However, as mentioned by Tsujimoto et al., the reduction and oxidation processes proceed via the brownmillerite-type intermediate $SrFeO_{2.5}$[7], which has a similar cation arrangement as in $SrFeO_2$ and $SrFeO_3$, but with tetrahedrally and octahedrally coordinated iron (Figure 2). Therefore, these reactions cannot be purely topotactic, and oxygen obviously has a high mobility in compounds of this system at low temperatures.

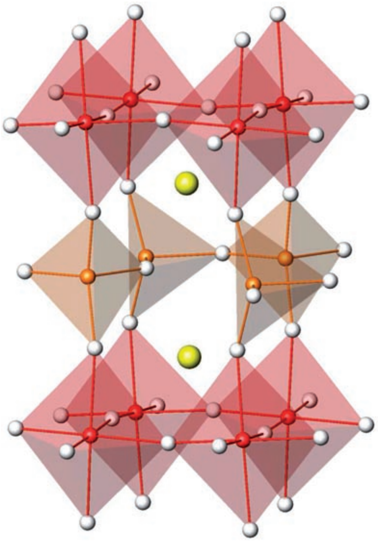

Figure 2. Perspective view of a section of the crystal structure of $SrFe_2O_5$. Fe(1) red, Fe(2) orange, Sr yellow, and O gray spheres. The coordination spheres around iron are graphically emphasized.

The layered strontium ferrate(II) $SrFeO_2$ is also very interesting because of its electronic and magnetic properties. The neutron powder diffraction patterns of $SrFeO_2$ reveal the presence of a three-dimensional (π,π,π) antiferromagnetic order, where the magnetic moments are perpendicular to the c and b axes (Figure 3). The temperature variations of the intensity of the magnetic peak in the neutron powder diagram give a Néel temperature ($T_N = 473$ K) that is even higher than that of FeO ($T_N \approx 200$ K) with a three-dimensional crystal structure. Such a high three-dimensional antiferromagnetic ordering temperature in a layered system is remarkable and unexpected, because T_N usually decreases drastically when the dimensionality decreases. From the neutron powder diffraction studies, the magnetic moment of $SrFeO_2$ has been found to be 3.1 μ_B per iron atom at 293 K and 3.6 μ_B at 10 K. The magnitude itself and its minor variation over the wide temperature range strongly suggest that the iron(II) ions are in the high-spin state. In accordance with the crystal field theory[20] the authors assumed a $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1$ configuration for the square-planar-coordinated iron(II) with a spin magnitude of $S = 4\,^1/_2 = 2$ (Figure 4a). However, if the lone down-spin electron of a high-spin iron(II) (d^6) ion at square-planar site occupies the degenerate (d_{xz},d_{yz}) orbitals, $SrFeO_2$ should be subject to orbital ordering or Jahn–Teller distortion when the temperature is lowered.[21] This is not the case and $SrFeO_2$ does not show any structural instability and maintains the space group $P4/mmm$ down to 4.2 K, which is also confirmed by ^{57}Fe Mössbauer spectroscopy.[8] Furthermore, the occupation of the (d_{xz},d_{yz}) orbitals with three electrons is not consistent with the fact that the magnetic moments lie perpendicular to the c axis.[22] The authors "believe that the orbital instability is overcome by the extremely strong covalency that favors directional and symmetrical Fe–O bonding".[8]

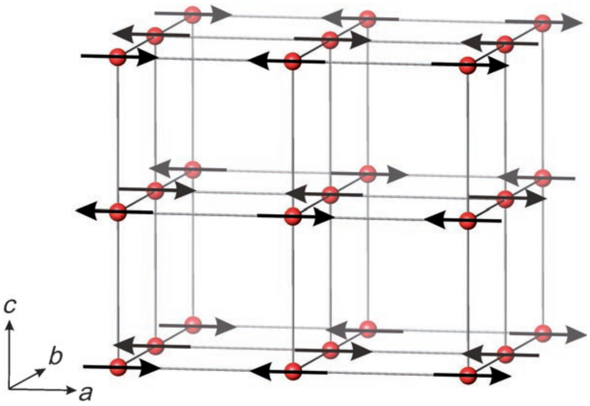

Figure 3. Magnetic 2×2×2 superstructure of $SrFeO_2$, with iron sites drawn as red circles. Arrows denote the direction of the magnetic moments.

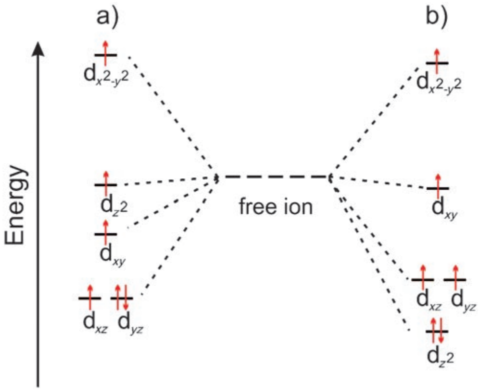

Figure 4. a) Assumed[8] and b) calculated[23] ligand field d-orbital splitting diagrams for the square-planar-coordinated iron(II) with high spin d^6 configuration in $SrFeO_2$.

Such puzzling abnormal structural and magnetic properties in $SrFeO_2$ call for an explanation, and shortly after the paper of Tsujimoto et al. appeared,[8] the magnetic properties of $SrFeO_2$ were examined by density functional theory (DFT) band structure and total energy calculations to evaluate its spin exchange interactions.[23] It was shown that the down-spin iron 3d electron occupies the nondegenerate d_{z^2} level rather than the expected degenerate (d_{xz}, d_{yz}) levels (Figure 4b).

Obviously in the layered structure of $SrFeO_2$, the energy of the d_{z^2} state is significantly decreased owing to reduced Coloumb repulsion, and this result explains the absence of a Jahn–Teller instability. Furthermore, Monte Carlo simulations using the extracted spin exchange parameters for the different pathways show that a strong interlayer spin exchange is essential for the high Néel temperature in $SrFeO_2$.[23]

To summarize, the new infinite-layer strontium ferrate(II) $SrFeO_2$ not only has an unusual structure with square-planar coordinated iron(II), but also exotic magnetic and electronic properties. The high mobility in the system $SrFeO_2$/$SrFeO_{2.5}$ at relatively low temperatures indicates that variants of $SrFeO_2$ might be useful for reducing the working temperatures of solid oxide fuel cells, membranes for oxygen separation, and sensor materials. It appears promising to investigate hole doping into the infinite-layer FeO_2 sheets of $SrFeO_2$—for example, by introducing selectively apical oxygen atoms at low temperatures, or by replacing strontium with a monovalent metal, such as sodium. Oxoferrates(I), such as K_3FeO_2,[24] are also known, and therefore, electron doping can even be imagined in $SrFeO_2$ by the substitution of strontium with a trivalent metal, such as lanthanum. Such materials based on $SrFeO_2$ can probably be tuned from one electronic or magnetic phase to another by varying the temperature or pressure, and might therefore be promising candidates for numerous applications.

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