

Structure and Magnetism of Infinite Layer Iron Oxide with a Square-Planar Coordination

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The coordination geometries more usually exhibited by iron in oxides are octahedral and tetrahedral.¹ However the use of calcium hydride as a low-temperature reductant, a technique recently introduced by Hayward, Rosseinsky and coworkers, has provided a way to circumvent this structural choice. For instance, Tsujimoto et al. have recently reported a new material, SrFeO₂, in which a high-spin Fe²⁺ exhibits a square-planar coordination. This material is built from unprecedented FeO₂ infinite layers in between which the Sr²⁺ cations reside (see Fig. 1(left)) and exhibits a number of surprising structural and physical properties. The study of the electronic structure of SrFeO₂ has provided important clues to understand this situation. Later, this material was shown to be remarkably robust towards cation substitution and temperature⁶ opening the way towards possible applications. More recently the same technique was used to prepare a new spin-ladder iron oxide, Sr₃Fe₂O₅, which again exhibits high-spin Fe²⁺ ions in a square-planar coordination.

The neutron diffraction study and the synchrotron X-ray diffraction revealed that CaFeO₂ exhibit an unprecedented layered structure [1]. The new phase was obtained through a low-temperature reduction procedure using calcium hydride. The XAS spectra near the Fe-K edge for the whole solid solution (Sr_{1-x}Ca_x)FeO₂ supports that iron is in a square-planar coordination for $0 < x < 0.8$ but clearly suggests a change of coordination for $x = 1$. The new structure contains infinite FeO₂ layers in which the FeO₄ units unprecedentedly distort from square-planar toward tetrahedra and rotate along the c axis (see Fig. 1(right)), in marked contrast

to well-studied and accepted concept that octahedral rotation in perovskite oxides occurs but the octahedral shape is kept almost regular.

[1] T. Cedric et al., J. Am. Chem. Soc. 131, 221-229 (2008).

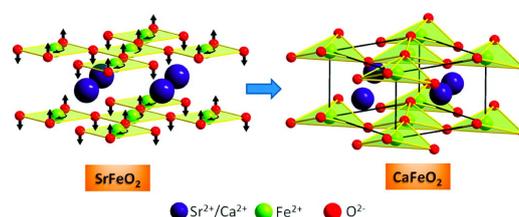


Fig. 1. Crystal structures of the ideal infinite structure SrFeO₂ (left) and the distorted one CaFeO₂ (right).