The concept of “spin ladder” originally appeared to study the theoretically still controversial antiferromagnet (AF) 2D square lattice in high-temperature superconducting cuprates starting from a well understood 1D AF chain [1-2]. They can be schematized as an array of finite number of coupled chains. The motivation of theoretical investigations has been to test how the one-dimensional (1D) S=1/2 AF chain system \((n=1)\), that is rigorously solved even when doped with carriers, could be connected to the 2D square lattice \((n=\infty)\) that in turn encounters various theoretical difficulties and is far from being understood. Experimentally, \(\text{Sr}_{1-x}\text{Cu}_x\text{O}_2\) has been the only example representing a 3D polyhedra precursor. For \(\text{Sr}_{1-x}\text{Fe}_x\text{O}_2\) the coordination geometries in iron oxides have been almost exclusively restricted to 3D polyhedra involving oxide ions. Unlike in the case of cuprates, the coordination geometries in iron oxides have almost exclusively restricted to 3D polyhedra such as octahedra and tetrahedra. However, this barrier has recently been overcome [7], using electropositive calcium hydride at low temperatures as a reductant, the low-temperature reaction of a cubic perovskite \(\text{SrFe}_{2+y}\text{O}_7\) with \(\text{CaH}_2\) stabilized \(\text{SrFe}_{2}\text{O}_7\) with a square-planar oxygen coordination around the high-spin \(\text{Fe}^{2+}\) ion. The structure is isostructural with the “infinite” layer cupric oxides. For the first time we show the synthesis of a novel spin-ladder iron oxide \(\text{Sr}_3\text{Fe}_2\text{O}_5\) through the reaction of the double-layered perovskite \(\text{Sr}_2\text{Fe}_2\text{O}_7\) with \(\text{CaH}_2\) [8]. By using neutron diffraction, synchrotron X-ray diffraction and Mössbauer, we provide a complete characterization of this first spin ladder iron oxide.

A slightly oxygen deficient phase \(\text{Sr}_3\text{Fe}_2\text{O}_{7-y}\) \((y<0.4)\) could be easily prepared by a conventional, high-temperature solid-state reaction and was used as a precursor. For \(\text{Sr}_3\text{Fe}_2\text{O}_{7-y}\) all oxygen vacancies are located at the apical O(1) sites shared by the double \(\text{FeO}_6\) sheets (Figure 1a and b) and the structure keeps the \(I4/mmm\) space group over the entire range from \(\text{Sr}_3\text{Fe}_2\text{O}_7\) \((y=0)\) to \(\text{Sr}_3\text{Fe}_2\text{O}_6\) \((y=1)\) [9].

The powder X-ray diffraction (XRD) pattern of the present precursor also indicated a tetragonal \(I4/mmm\) cell with \(a=3.872\) Å and \(c=20.157\) Å. To prepare \(\text{Sr}_3\text{Fe}_2\text{O}_6\), \(\text{Sr}_3\text{Fe}_2\text{O}_{6.4}\) \((0.43\text{ g})\) and a two-molar excess of \(\text{CaH}_2\) were finely ground and pelletized in an argon-filled drybox, sealed in an evacuated glass tube, and brought to reaction at 623 K for 3 days. The final product was washed to remove undesirable residues, \(\text{CaH}_2\) and \(\text{CaO}\), with a dried 0.1 M \(\text{NH}_4\text{Cl/methanol solution. The Fe-oxide thus obtained is quite air-sensitive so that all the chemical and physical characterizations were conducted with efforts to minimize exposure to air. Synchrotron powder XRD pattern of the final product taken at the SPring-8 (Japan) BL02B2 beam line \((\lambda=0.777\) Å) showed that \(\text{Sr}_3\text{Fe}_2\text{O}_5\) adopts the \(I4/mmm\) space group (No. 71), with \(a=3.51685(5)\) Å, \(b=3.95405(7)\) Å, \(c=20.91672(36)\) Å. Neutron powder diffraction (DIA at ILL and G4.1 at the LLB) analysis at 293 K confirmed the above structure and it also excluded a possibility that hydrogen atoms are incorporated into the lattice. Furthermore, Mössbauer measurements (Figure 2a) indicated not only that all the Fe atoms are electronically and
crystallographically equivalent, but also that they are most likely square-planar coordinated in high-spin state (S=2), since the obtained isomer shift (IS) of 0.46 mms⁻¹, quadrupole splitting AE of 1.28 mms⁻¹ at 300 K, and the magnetic hyperfine field of H_m=43.7 T at 4 K are close to those of SrFeO₂ [9]. These observations are consistent with the structural analysis. Neutron powder diffraction data down to 1.4 K on G41 (LLB, λ=2.42 Å) (Figure 2b) and D1A (ILL, λ=1.91 Å) revealed that the long-range AF order is characterized by a magnetic propagation vector q= (1/2, 1/2, 0) and that the iron moments of 2.76(5) µ_B are aligned parallel to the c axis.

Finally, we must assume that the present synthetic strategy involving CaH₂ reduction can be further generalized for a more rational design of new magnetic lattices comprising extended arrays of FeO₄ square planes, for which formerly only copper(II) oxides were candidates.

References:

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