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Minfeng Lü, Olivier Mentre, Elijah E. Gordon, Myung-Hwan Whangbo, Alain Wattiaux, et al.. A comprehensive study of magnetic exchanges in the layered oxychalcogenides  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  ( $\text{Q} = \text{S}, \text{Se}$ ). *Journal of Magnetism and Magnetic Materials*, 2017, 444, pp.147-153. 10.1016/j.jmmm.2017.07.026 . hal-01611341

**HAL Id: hal-01611341**

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Submitted on 13 Sep 2021

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# A comprehensive study of magnetic exchanges in the layered oxychalcogenides $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$ ( $Q = \text{S}, \text{Se}$ )

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## A B S T R A C T

The layered oxysulfide  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  was prepared, and its crystal structure and magnetic properties were characterized by synchrotron X ray diffraction (XRD), powder neutron diffraction (PND), Mössbauer spectroscopy measurements and by density functional theory (DFT) calculations. In addition, the spin exchange interactions leading to the ordered magnetic structure of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  were compared with those of its selenium analogue  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$ . The oxysulfide  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  adopts a G type antiferromagnetic (AFM) structure at a temperature in the range 485–512 K, which is comparable with the three dimensional (3D) AFM ordering temperature,  $T_N \approx 490$  K, found for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$ . Consistent with this observation, the spin exchange interactions of the magnetic  $(\text{Sr}_3\text{Fe}_2\text{O}_5)^{2+}$  layers are slightly greater (but comparable) for oxysulfide than for the oxyselenide. Attempts to reduce or oxidize  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  using topochemical routes yield metallic Fe.

### Keywords:

Layered oxychalcogenides  
Antiferromagnetism  
Mössbauer  
Neutron diffraction  
Magnetic structure

## 1. Introduction

In recent years, layered oxychalcogenides in which oxide layers alternate with chalcogenide layers have received much attention because of their tunable properties [1–3], from optical properties [4,5] as found for the wide gap p type semiconductors  $\text{LaCuOQ}$  ( $Q = \text{S}, \text{Se}$ ) [6,7] to various magnetic behaviors [8]. Since a specific layer can be chemically modified, the properties of these compounds are more readily tuned compared with those of three dimensional (3D) compounds [9,10]. As demonstrated for the series  $\text{Sr}_{n+1}\text{M}_n\text{O}_{3n-1}\text{Cu}_{2m}\text{Q}_{m+1}$ , which consists of  $\text{Cu}_{2m}\text{Q}_{m+1}$  chalcogenide and  $\text{Sr}_{n+1}\text{M}_n\text{O}_{3n-1}$  oxide ( $n = 1–3$ ) layers [9,12], the oxide sublayer can be modified in a topochemical manner. The reduction of  $\text{Sr}_4\text{Mn}_3\text{O}_8\text{Cu}_2\text{Q}_2$  ( $n = 3, m = 1$ ) by oxygen deintercalation using hydrides or by oxidation using fluorination modifies the  $\text{Sr}_4\text{Mn}_3\text{O}_8$  magnetic layer [11]; the reduction destroys the magnetic long range order through an increased chemical disorder whereas the

fluorination strengthens the AFM interactions without changing the chalcogenide layers. The magnetic properties of  $\text{Sr}_{n+1}\text{M}_n\text{O}_{3n-1}\text{Cu}_{2m}\text{Q}_{m+1}$  depend on the values of  $n$  and  $m$ , i.e., the thickness of the chalcogenide and oxide layers. The iron based oxysulfide  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  was first prepared by Zhu et al. [13]. As depicted in Fig. 1, it is related to this family (i.e.,  $n = 2$  and  $m = 1$ ). A subsequent study showed that the  $(\text{Cu}_2\text{S}_2)$  layers can be replaced with  $(\text{Cu}_2\text{Se}_2)$ ,  $(\text{Ag}_2\text{S}_2)$ ,  $(\text{Ag}_2\text{Se}_2)$  or  $(\text{Zn}_2\text{P}_2)$  layers [14]. The selenide analogue  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$  was synthesized and fully characterized. A  $^{57}\text{Fe}$  Mössbauer study combined with PND measurements revealed the onset of an AFM order at  $T_N \approx 490$  K [14]. This high  $T_N$  falls well above the ordering temperature range expected for a 2D magnetic compound, in good agreement with the 3D magnetic behavior deduced from the value of  $\beta \approx 0.3$  fitted for  $M(T) \propto C(1 - T/T_N)^\beta$ . It suggests the presence of long range dipole-dipole interactions due to the separation between the blocks. In contrast, the magnetic properties of the sulfur analogue  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  have not been characterized yet. In the present work, we explore the magnetic properties of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  by PND and Mössbauer measurements and compare them with those of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$ , after examination of the spin exchange interactions of both compounds on the basis of density functional theory (DFT) calculations to account for their ordered magnetic structures below  $T_N$ .

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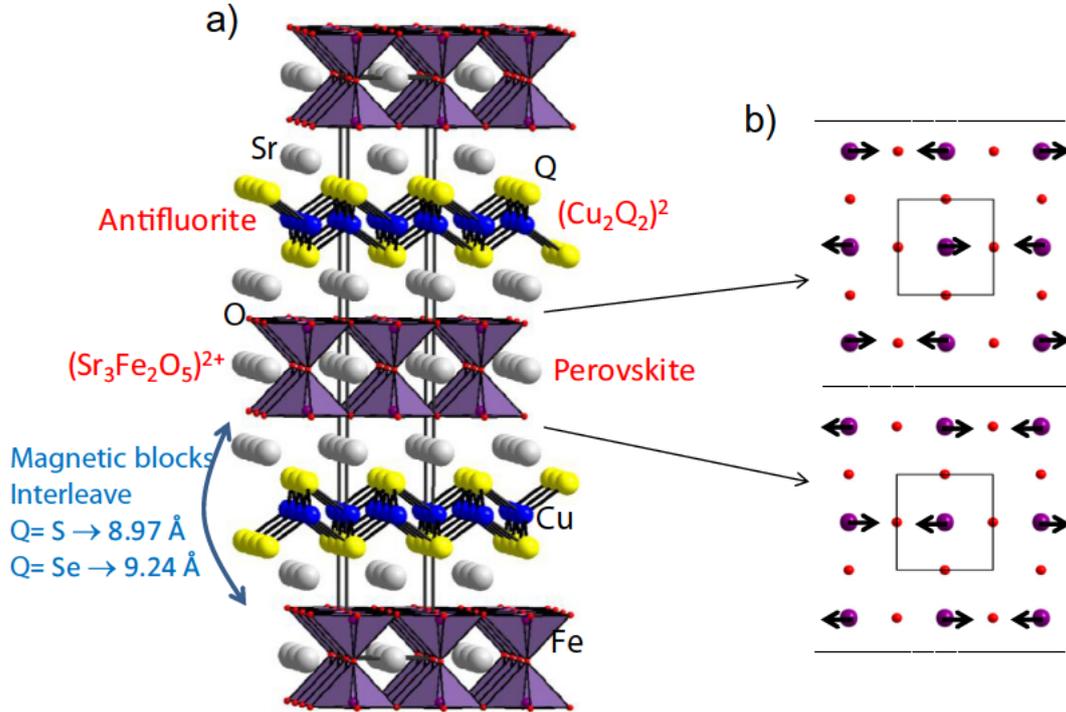


Fig. 1. a) Structure of the phases  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = S, Se). b) Schematic representation of the G-type AFM structure, where each Fe layer is represented by a projection view on the ab plane.

## 2. Experimental

Polycrystalline samples of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  were prepared by a standard solid state synthesis, as reported in Ref. [13]. First,  $\text{SrCuO}_2$  was obtained by reacting  $\text{SrCO}_3$  and  $\text{CuO}$ . Then, stoichiometric amounts of  $\text{SrS}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{SrCuO}_2$  were ground in a glove box, pressed into pellets and sealed in an evacuated quartz tube. The pellets were heated to  $800^\circ\text{C}$  at a rate of  $100^\circ\text{C/h}$  and maintained at this temperature for 48 hours before the furnace was switched off. It was not possible to prepare  $\text{Sr}_3\text{Fe}_2\text{Cu}_2\text{S}_2\text{O}_5$  without minute amount of  $\text{Fe}_3\text{O}_4$  impurity. The purity of the precursors was checked using standard laboratory X ray diffraction (XRD). Synchrotron XRD measurements at room temperature were performed at the 11BM beamline (APS, Argonne National Lab, US) using the wavelength  $\lambda = 0.413967 \text{ \AA}$ . PND measurements were carried out at the Laboratoire Leon Brillouin (LLB) Saclay on the 3T2 diffractometer ( $\lambda = 1.2254 \text{ \AA}$ ). The Powder XRD and PND data were analyzed using the Rietveld method encoded in the FULLPROF 2000 suite [15]. Depending on the sample either minor amounts of  $\text{SrSO}_4$ ,  $\text{Sr}_7\text{Fe}_{10}\text{O}_{22}$  (negligible) or  $\text{Fe}_3\text{O}_4$  have been identified and taken into account in the refinements.

$^{57}\text{Fe}$  Mössbauer measurements were performed using a constant acceleration Halder type spectrometer with a room temperature  $^{57}\text{Co/Rh}$  source in transmission geometry. The spectra were recorded from room temperature up to  $512 \text{ K}$  using a homemade furnace and the velocity scale was calibrated according to the  $^{57}\text{Fe}$  Mössbauer spectrum of a pure  $\alpha$  Fe foil. Both homemade programs and the WinNormos<sup>®</sup> software were used for the analysis of  $^{57}\text{Fe}$  Mössbauer spectra.

The transport measurements were carried out on a home made four probe apparatus using a dense bar pressed sample sintered at  $800^\circ\text{C}$ . The resistivity was calculated by taking into account the shape and the size of the sample.

## 3. Experimental results

In  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$ , the  $(\text{Sr}_3\text{Fe}_2\text{O}_5)^{2+}$  magnetic layers containing high spin  $\text{Fe}^{3+}$  ( $S = 5/2$ ,  $d^5$ ) ions alternate with the  $(\text{Cu}_2\text{S}_2)^2$  diamagnetic layers containing nonmagnetic ions  $\text{Cu}^+$  ( $d^{10}$ ), see Fig. 1. Our refinement based on the synchrotron XRD (Fig. 2c) led to the structural parameters, atomic positions and anisotropic thermal parameters reported in Tables 1 and 2 ( $R_{\text{Bragg}} = 3.47\%$ ,  $\chi^2 = 1.47$ ). We note that  $\text{SrSO}_4$  ( $\sim 2 \text{ wt\%}$ ) was also detected and refined together with minor unidentified peaks. Previous studies reported the deficiency of Cu in the  $(\text{Cu}_2\text{Q}_2)$  layers and possible cationic and anionic vacancies in the perovskite layers [9,11] in good agreement with its 93% occupancy refined from XRD data. Our Rietveld refinement of the PND data (Fig. 2a and b) shows that the Cu site shows significant deficiency leading to its occupancy of 94%. The structural refinement converged to the neutral formula  $\text{Sr}_3\text{Fe}_2\text{O}_{4.94}\text{Cu}_{1.89}\text{S}_2$ , in which oxygen vacancies are located at the O2 atoms (i.e., the apical shared O atoms of two  $\text{FeO}_5$  square pyramids, see Fig. 1). The refined lattice parameters are  $a = 3.9182(1) \text{ \AA}$  and  $c = 26.3617(7) \text{ \AA}$  with  $R_{\text{Bragg}} = 3.18\%$ . In the concerned sample ( $\sim 2 \text{ g}$ ),  $\text{Fe}_3\text{O}_4$  was detected ( $\sim 3 \text{ wt\%}$ ) and refined. We however could not identify copper containing impurity as would be expected, probably due to crystallinity and weak scattering power. The refinement converged only after considering the magnetic structures of both  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  and the impurity  $\text{Fe}_3\text{O}_4$  as detailed below.

The essential structural features of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) are shown in Fig. 1. The magnetic  $\text{Sr}_3\text{Fe}_2\text{O}_5$  layer is made up of  $\text{FeO}_5$  square pyramids containing high spin  $\text{Fe}^{3+}$  ions. Every two  $\text{FeO}_5$  square pyramids share their apical O2 atoms to form  $\text{Fe}_2\text{O}_9$  dumbbells, which share their basal O1 atoms to form the  $\text{Fe}_2\text{O}_5$  double layer. An obvious difference between the oxysulfide and the oxyselenide is that the distance separating the magnetic layers ( $\text{Sr}_3\text{Fe}_2$

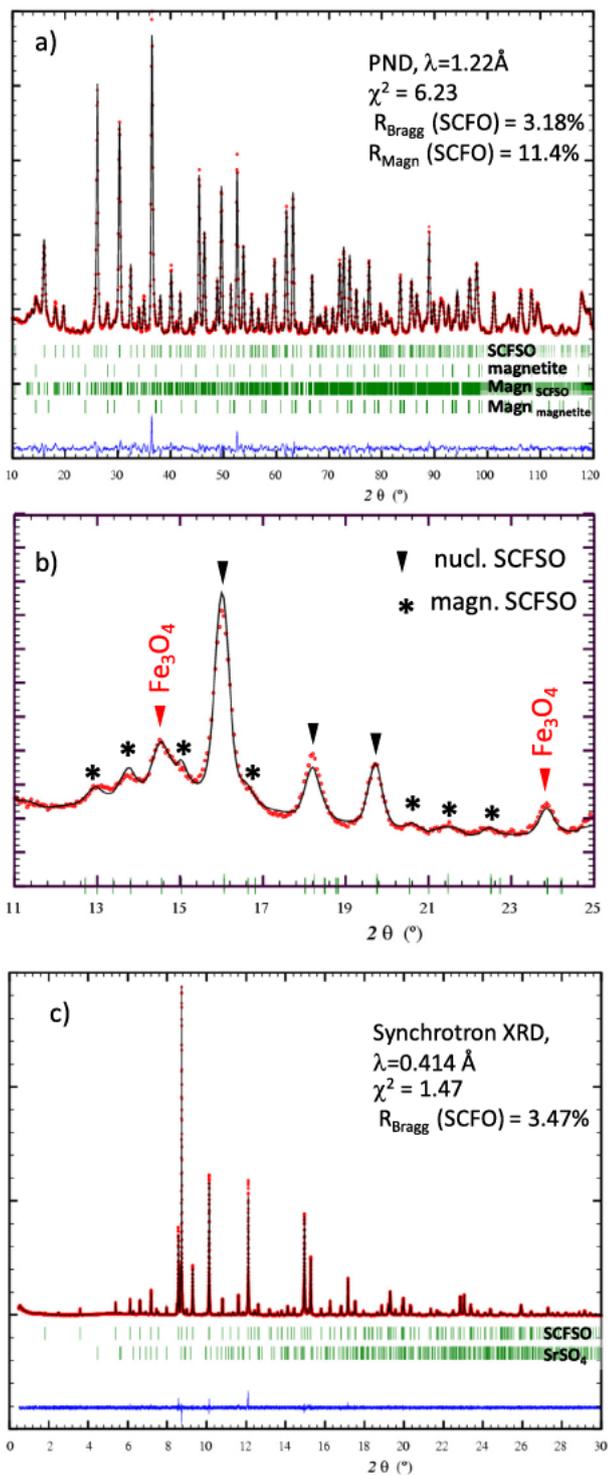


Fig. 2. a–b) Neutron diffraction pattern recorded for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  (open circles). The black line represents the calculated intensities. The bottom curve is the difference between the experimental and calculated intensities. The small marks indicate the Bragg peak positions of the main phase and impurity. c) X-ray Synchrotron diffraction patterns recorded for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  (open circles). The red line represents the calculated intensities by the Rietveld method. The bottom curve is the difference between the experimental and calculated intensities. The small marks indicate the Bragg peak positions of the main phase and impurity.

$O_5$ ) increases from 8.99 Å for Q = S to 9.24 Å for Q = Se. It was determined between the layers made up of the basal  $O_1$  atoms and from our PND refinement for Q = Se. In contrast, the Fe environment is almost unchanged considering the distances in the  $\text{FeO}_5$  pyramids

(see Table 4), and the in plane  $\angle \text{Fe O Fe}$  angles of  $165.1^\circ$  in both compounds.

The PND data collected at room temperature for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  show magnetic satellites in the low angle region in addition with the magnetic satellites belonging to  $\text{Fe}_3\text{O}_4$ . They are indexed using the propagation vector  $k = (\frac{1}{2}, \frac{1}{2}, 0)$ , as observed for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$  [14]. We found a G type AFM arrangement as reported for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$  with the moment lying in the ab plane (Fig. 1) and parallel to a or b direction by equivalence. At room temperature, the refined moment is  $1.57(3) \mu_B/\text{Fe}$  with  $R_{\text{magn}} = 11.4\%$ , which is well below the  $5 \mu_B/\text{Fe}$  value expected for the high spin  $\text{Fe}^{3+}$  ion. One assumption could be related to O deficiency that may break some of the exchange pathways and possibly lead to frustration. However, the phase presents rather low deficiency (95% occupancy for  $O_2$ ). In addition, we note that for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$ , the refined moment is also below the expected one even at low temperature (2 K), i.e.  $3.6(2) \mu_B/\text{Fe}$  [14]. As an explanation, it is argued that  $\text{Fe}^{3+}$  could be partly involved in a short range magnetic ordering. Taking into account the  $\beta \sim 0.3$  critical exponent [16] fitted for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$  ( $T_N = 490 \text{ K}$ ) [14], the value of the refined iron moment suggests similar  $T_N$ . However, dealing with room temperature PND data in our study, the accurate estimation of  $T_N$  is difficult since the magnetization is strongly affected even at high temperature by the presence of  $\text{Fe}_3\text{O}_4$ , see the Supporting information (SI).

The accurate determination of  $T_N$  of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  was performed by  $^{57}\text{Fe}$  Mössbauer analysis versus temperature. The spectrum recorded at room temperature and at high velocity scale is shown in Fig. 3. The experimental data are well refined (Table 3) by using three components (denoted D1, D2 and S3). The main sextet contribution D1 (about 87%) arises from the  $\text{Fe}^{3+}$  ions of a magnetically ordered compound. We simulate the D1 signal by using a distribution of the hyperfine magnetic field parameter (H), i.e., a sum of sextets with same isomer shift ( $\delta$ ) and quadrupole shift ( $\varepsilon$ ) but different values of H, to reflect slight variations of the magnetic environments of the  $\text{Fe}^{3+}$  ions. The D1 sextet confirms that the  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  phase is magnetically ordered at room temperature, as proposed above by analogy with the selenium analogue. The second component D2 (about 8% in relative area) can be assigned to the  $\text{Fe}^{3+}$  ions of one of the iron containing impurities, for instance  $\text{Sr}_7\text{Fe}_{10}\text{O}_{22}$  that does not order magnetically at room temperature (see Section 3). In this impurity phase, some heterogeneity in the Fe O bond distances and/or some disorder in the environment of  $\text{Fe}^{3+}$  ions can induce significant variations of the electric field gradient (EFG) experienced by the iron nuclei. This would explain why a multimodal character of the quadrupole splitting distribution was necessary to simulate this second component (see Fig. 3). In addition to the D1 and D2 contributions, the presence of a third magnetic component, S3, was assigned to a small amount of  $\text{Fe}_3\text{O}_4$  impurity. The latter is magnetic at room temperature and undergoes a ferrimagnetic transition around  $T_c \approx 848 \text{ K}$ . Even if it is assumed that D1 and D2 are the major phases, their relative ratio cannot be reliably determined because they have different Lamb Mössbauer f factors.

The  $^{57}\text{Fe}$  Mössbauer spectra recorded at various temperatures from 293 to 512 K are presented in Fig. 4. With increasing the temperature, the main component D1 of the Mössbauer spectrum evolves from a magnetic sextet to a paramagnetic quadrupole doublet. Then, the magnetic ordering of the main phase  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  occurs between  $T_N = 485$  and 512 K. The influence of the temperature increase (up to 512 K) on the components D2 and S3 is difficult to explain due to the low signal to noise ratio of the measurements performed at high temperature. Nevertheless, the external peaks of the S3 sextet are still at 512 K (Fig. 4) after long time collection, in good agreement with what is expected for  $\text{Fe}_3\text{O}_4$ .

**Table 1**  
Atomic positions of  $\text{Sr}_3\text{Fe}_2\text{O}_5-x\text{Cu}_2-y\text{S}_2$  from synchrotron/neutron data refinement.

Atom	x	y	z	$B_{\text{eq}}$ or $B_{\text{iso}}$	Occ_site
Sr1	0	0	0.5	0.98 $e_q/0.95(5)_{\text{iso}}$	1_2(b)
Sr2	0	0	0.6414(1)/0.64168(6) <sup>*</sup>	0.78 $e_q/0.53(2)_{\text{iso}}$	1_4(e)
Cu1	0	0.5	0.25	1.42 $e_q/1.12(4)_{\text{iso}}$	0.934(1)/0.94(1) <sup>*</sup> _4(d)
Fe1	0	0	0.0715(1)/0.07142(4) <sup>*</sup>	0.83 $e_q/0.41(2)_{\text{iso}}$	1_4(e)
S1	0	0	0.1959(1)/0.1958(2) <sup>*</sup>	1.022(23) <sub>iso</sub> /0.42(6) <sub>iso</sub>	1_4(e)
O1	0	0.5	0.0812(1)/0.08114(5) <sup>*</sup>	0.624(28) <sub>iso</sub> /0.74(2) <sub>iso</sub>	1/0.997(6) <sup>*</sup> _8(g)
O2	0	0	0	0.624(28) <sub>iso</sub> /0.74(2) <sub>iso</sub>	1/0.95(1) <sup>*</sup> _2(a)

<sup>\*</sup> From PND refinement; Unit cell parameters from synchrotron/neutron:  $a = 3.9211/3.9182(1)\text{\AA}$  and  $c = 26.3739/26.3617(7)\text{\AA}$  in space group  $I4/mmm$ .

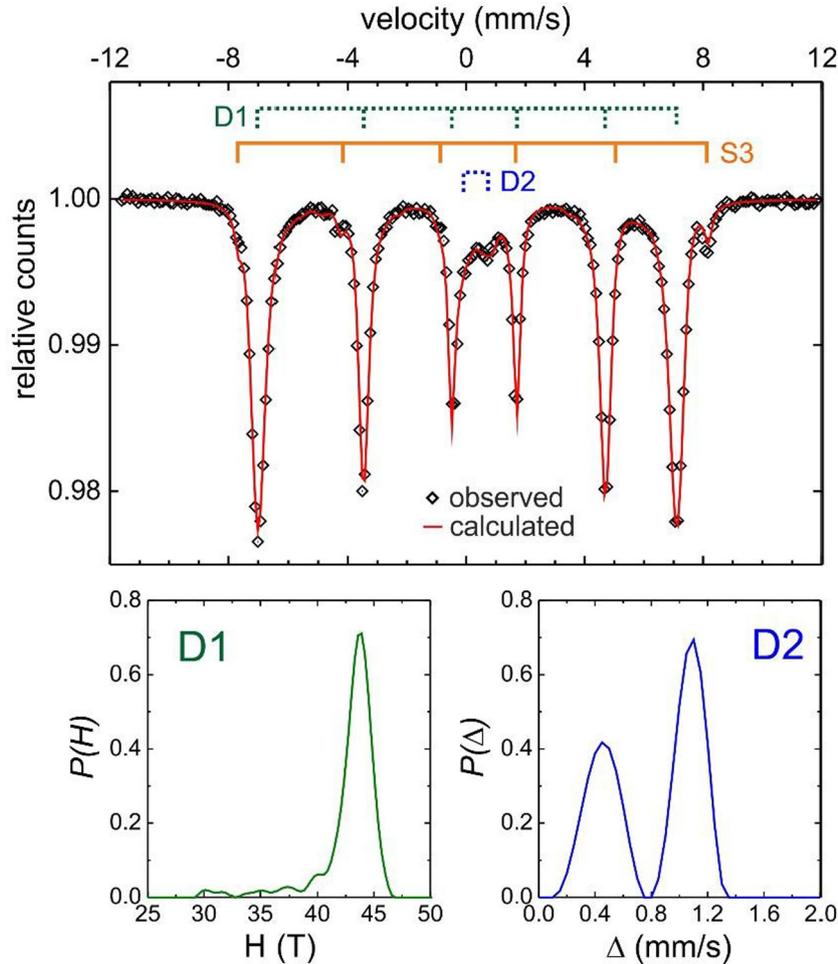
**Table 2**  
Anisotropic thermal parameters for the title compound from synchrotron data refinement in  $\text{\AA}^2$ . By symmetry we have:  $\beta_{11} = \beta_{22}$  and  $\beta_{12} = \beta_{13} = \beta_{23} = 0$ .

Atom	$\beta_{11} (\times 10^4)$	$\beta_{23} (\times 10^4)$
Sr1	85(2)	6.8(1)
Sr2	94(2)	3.8(1)
Cu1	246(3)	4.5(1)
Fe1	81(33)	5.4(1)

The resistivity of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  measured as a function of temperature is shown in Fig. 5, typical of a semiconductor behavior. Two weak anomalies at 100 and 330 K are detected. The intrinsic origin of the one at 330 K is questionable, but is far below the magnetic ordering,  $T_N$  being in the range 485–512 K. Then, the origin of

this anomaly is difficult to assess in the present study because of the ferromagnetic  $\text{Fe}_3\text{O}_4$  impurity that is present in low amount despite our efforts. To overcome this issue, alternative synthesis routes should be investigated to avoid its formation and thus obtain clean physical measurements but are out of the scope of this work.

The second one at 100 K is assigned to the Verwey transition of the  $\text{Fe}_3\text{O}_4$  second phase. This transition is visible in our low temperature magnetic measurements with a shape of  $\chi$  versus temperature typical of those reported for  $\text{Fe}_3\text{O}_4$ , see [Supplementary information](#). At both sides of this transition, data are well reproducing an Arrhenius law with similar calculated activation energies above and below 100 K, i.e.  $E_a = 0.08$  and  $0.06$  respectively.



**Fig. 3.** Room temperature  $^{57}\text{Fe}$  Mössbauer spectrum of  $\text{Sr}_3\text{Fe}_2\text{Cu}_2\text{S}_2\text{O}_5$ . The main magnetic component D1 and the non-magnetic (at room temperature) signal D2 were calculated using the distribution of the hyperfine magnetic field ( $H$ ) and the quadrupole splitting ( $\Delta$ ), respectively.

**Table 3**

$^{57}\text{Fe}$  Mössbauer hyperfine parameters determined from the analysis of  $\text{Sr}_3\text{Fe}_2\text{CuS}_2\text{O}_5$  spectrum (Fig. 3).  $\delta$ : isomer shift relative to  $\alpha\text{-Fe}$  at ambient temperature,  $\Delta$ : quadrupole splitting,  $\varepsilon$ : quadrupole shift,  $H$ : hyperfine magnetic field,  $\Gamma$ : line width and  $A$ : relative area.  $^{\circ}$ Mean value of the distribution of hyperfine magnetic field or quadrupole splitting parameter.

	$\delta$ (mm/s)	$2\varepsilon$ (mm/s)	$\Delta$ (mm/s)	$H$ (T)	$\Gamma$ (mm/s)	$A$ (%)
D1	0.336(2)	-0.557(3)	-	42.8 $^{\circ}$	0.30(-)	87(2)
D2	0.323(4)	-	0.81 $^{\circ}$	-	0.30(-)	8(2)
S3	0.30(2)	-0.07(2)	-	49.1(2)	0.32(2)	5(2)

**Table 4**

Geometrical parameters associated with the exchange paths  $J_1$ - $J_4$  of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$ . The numbers in and outside parentheses are for Q = S and Se, respectively.

	Fe...Fe (Å)	Fe-O...O-Fe (Å)	O...O (Å)	$\angle\text{Fe-O-Fe}$ ( $^{\circ}$ )
$J_1$	3.958 (3.912)	1.996, 1.996 (1.967, 1.967)	-	165.1 (167.7)
$J_2$	3.739 (3.779)	1.870, 1.870 (1.889, 1.889)	-	180.0 (180.0)
$J_3$	5.597 (5.532)	1) 1.996, 1.996 (1.967, 1.967) 2) 1.996, 1.996 (1.967, 1.967)	1) 2.799 (2.766) 2) 2.799 (2.766)	-
$J_4$	5.445 (5.439)	1) 1.996, 1.870 (1.967, 1.889) 2) 1.870, 1.996 (1.889, 1.967)	1) 2.906 (2.870) 2) 2.906 (2.870)	-

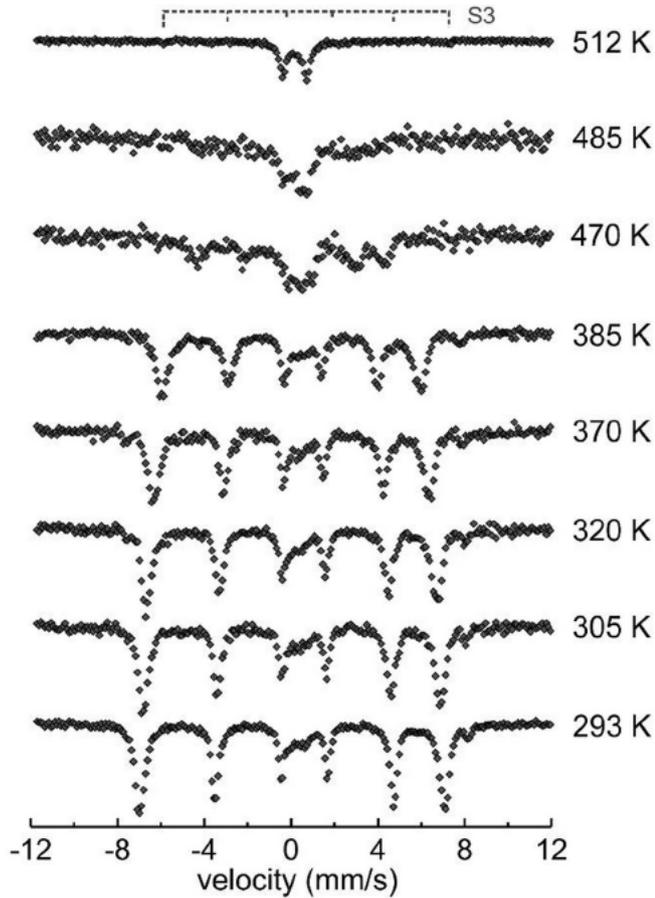


Fig. 4.  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Sr}_3\text{Fe}_2\text{CuS}_2\text{O}_5$  recorded as a function of temperature from room temperature to 512 K. The duration of data collection is twice longer for the 512 K spectrum (five days) than for other temperature spectra.

To see the possibility of tuning the magnetic properties of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$ , topochemical reactions were carried out to see if the magnetic properties of the  $\text{Sr}_3\text{Fe}_2\text{O}_5$  layers can be directly altered by creating O vacancies or by replacing  $\text{O}^{2-}$  by F. A topochemical reduction with hydride  $\text{CaH}_2$  and a topochemical oxidation with polyvinylidene fluoride (PVDF) were attempted as described in Ref. [11]. However, both attempts yielded Fe metal (clearly identified from Mössbauer spectroscopy) without softly altering the Fe environment and its oxidation state.

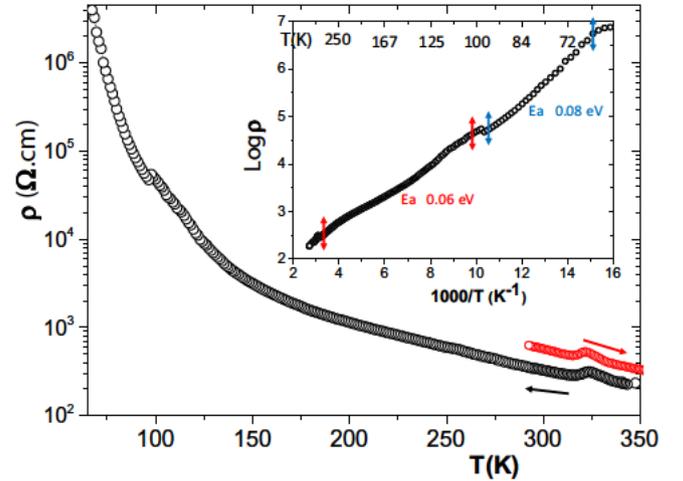


Fig. 5. Resistivity of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  as a function of temperature. The inset shows the activation energies extraction.

#### 4. Magnetic exchanges in $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$ (Q = Se, S)

The magnetic layer  $\text{Sr}_3\text{Fe}_2\text{O}_5$  of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  has two different Fe O Fe ( $J_1$  and  $J_2$ ) and two different Fe O...O Fe ( $J_3$  and  $J_4$ ) spin exchange paths as depicted in Fig. 6. The geometrical parameters associated with these exchange paths are summarized in Table 4. To evaluate the spin exchange parameters  $J_1$ - $J_4$ , we used the energy mapping analysis based on DFT electronic structure calculations [17,18]. We carry out spin polarized DFT calculations by employing the projector augmented wave (PAW) method encoded in the Vienna ab initio simulation package (VASP) [19-21] and the generalized gradient approximation of Perdew, Burke and Ernzerhof for the exchange correlation functionals [22]. The plane wave cutoff energies of 520 eV and the threshold of self consistent field energy convergence of  $10^{-6}$  eV were used. We employed the DFT plus on site repulsion U (DFT+U) method [23] to describe the electron correlation associated with the 3d states of Fe using the effective on site repulsion  $U_{\text{eff}} = U - J = 4, 5$  eV. The spin exchange parameters were extracted by using a (2a, 2b, c) super cell with a set of  $3 \times 3 \times 1$  k points. The preferred spin orientations of the  $\text{Fe}^{3+}$  ions in  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) were calculated by performing DFT+U calculations with spin orbit coupling (SOC) effect included [24].

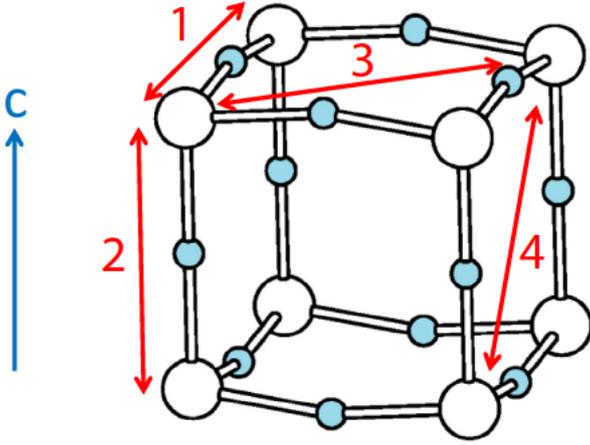


Fig. 6. Four spin exchanges  $J_1$ – $J_4$  of the  $\text{Sr}_3\text{Fe}_2\text{O}_5$  layer in  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S). The numbers 1–4 refer to  $J_1$ – $J_4$ , respectively.

To determine the values of  $J_1$ – $J_4$  intra-layer exchanges using the energy mapping analysis, we consider five ordered spin states FM, AF1, AF2, AF3 and AF4 defined by using a (2a, 2b, c) supercell (Fig. 7) and determine their relative energies on the basis of DFT+U calculations. The calculated relative energies of these states are summarized in Table S2 of the Supporting information (SI). To extract the values of  $J_1$ – $J_4$  from the above electronic structure calculations, we express the total spin exchange interaction energies of the five ordered spin states in terms of the Heisenberg spin Hamiltonian,

$$\hat{H} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (1)$$

where  $J_{ij} = J_1$ – $J_4$  is the spin exchange parameters between the spin sites  $i$  and  $j$ , and  $\hat{S}_i$  and  $\hat{S}_j$  are the spin operators at the spin sites  $i$  and  $j$ , respectively. Then, for each of the five ordered spin states, the total spin exchange energy per (2a, 2b, c) supercell, i.e., per 8 formula units (FUs), can be written as

$$E = (n_1 J_1 + n_2 J_2 + n_3 J_3 + n_4 J_4) (N^2 / 4) \quad (2)$$

by applying the energy expressions obtained for spin dimers with  $N$  unpaired spins per spin site [17,18]. In the present case,  $N = 5$  for the high spin  $\text{Fe}^{3+}$  ions. The magnetic moment of  $\text{Fe}^{3+}$ , found from our DFT+U calculations with  $U_{\text{eff}} = 4$  eV for the ferromagnetic state of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$ , is  $4.28 \mu_B$  for Q = Se, and  $4.29 \mu_B$  for Q = S. ( $4.36$  and  $4.37 \mu_B$  with  $U_{\text{eff}} = 5$  eV). These results are consistent with the presence of high spin  $\text{Fe}^{3+}$  ions in  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S). The coefficients  $n_1$ – $n_4$  for the five spin ordered states are summarized in Table S3. By mapping the relative energies of the five spin ordered states onto the corresponding energies expected from the total spin exchange energies, we obtain the values of  $J_1$ – $J_4$  summarized in Table 5.

All four spin exchanges are AFM, the two Fe–O–Fe exchanges  $J_3$  and  $J_4$  are negligible compared with the two Fe–O–Fe exchanges  $J_1$  and  $J_2$ , and  $J_2$  is stronger than  $J_1$ . In agreement with experiments, these spin exchanges predict that the ordered magnetic structure for the  $\text{Sr}_3\text{Fe}_2\text{O}_5$  layer is the one in which the AFM dimers defined by  $J_2$  (i.e., the  $\text{Fe}_2\text{O}_9$  dumbbells) are antiferromagnetically coupled to form a G type AFM structure for the  $\text{Sr}_3\text{Fe}_2\text{O}_5$  oxide layer. Note that the spin exchange values are rather similar for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  and  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$  in good agreement with their close  $T_N$  values. The distance between adjacent  $\text{Sr}_3\text{Fe}_2\text{O}_5$  in  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) ( $8.99 \text{ \AA}$  for Q = S and  $9.24 \text{ \AA}$  for Q = Se) is too large for the magnetic orbitals of one layer to overlap with those of its adjacent layer. Thus, the 3D AFM ordering in  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S), which requires interactions between the magnetically ordered  $\text{Sr}_3\text{Fe}_2\text{O}_5$  layers, is due most likely to the magnetic dipole-dipole (MDD) interactions [25–27], which are long range interactions.

Finally, we examine the preferred spin orientations of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) by performing DFT+U+SOC calculations for their ferromagnetic state. These calculations show that the spin orienta

Table 5

Values of the exchange constants  $J_1$ – $J_4$  (in meV) of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  determined from energy-mapping analysis on the basis of DFT+U calculations with  $U_{\text{eff}} = 4$  and 5 eV. The numbers in and outside parentheses are for Q = S and Se, respectively.

	$U_{\text{eff}} = 4$ eV	$U_{\text{eff}} = 5$ eV
$J_1$	–7.77 (–8.46)	–6.52 (–0.79)
$J_2$	–17.85 (–18.27)	–15.54 (–15.58)
$J_3$	–0.44 (–0.49)	–0.34 (–0.37)
$J_4$	–0.57 (–0.62)	–0.45 (–0.48)

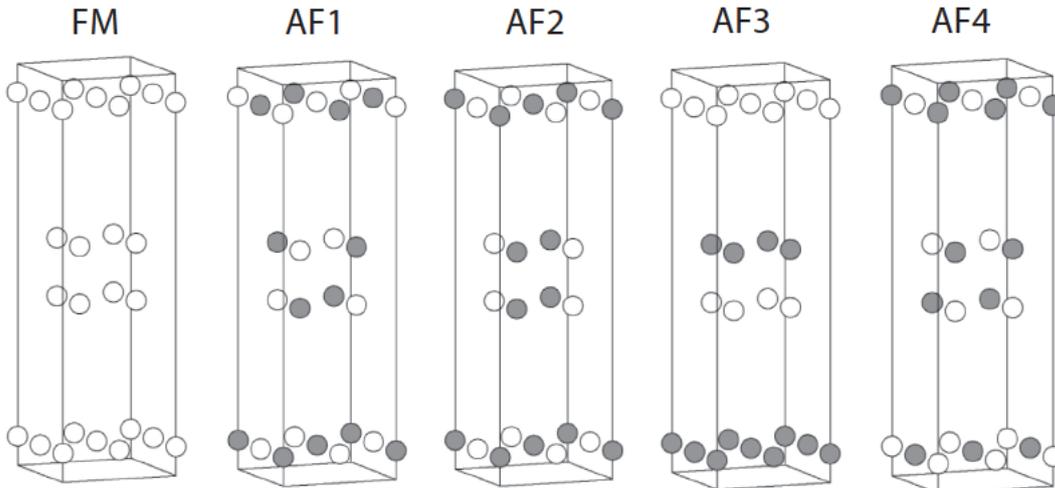


Fig. 7. Five ordered spin states of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) defined using a (2a, 2b, c) supercell. Only the  $\text{Fe}^{3+}$  ion sites are shown. The unshaded and shaded circles represent the up-spin and down-spin  $\text{Fe}^{3+}$  ion sites, respectively.

tion parallel to the *ab* plane is more stable than that perpendicular to the *ab* plane by 0.33 and 0.25 meV/unit cell (i.e., two FUs) for Q = Se and S, respectively. This is in agreement with the experimental observations.

## 5. Conclusion

In summary, the oxysulfide  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  shows a Cu deficiency in the ( $\text{Cu}_2\text{S}_2$ ) layer leading to the stoichiometry  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_{1.89}\text{S}_2$ , as found for other members of the homologous series  $\text{Sr}_{n+1}\text{MO}_{3n-1}\text{Cu}_{2m}\text{X}_{m+1}$ . The calculated spin exchange parameters reveal that the magnetic structures of  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) are dominated by the two Fe O Fe spin exchanges  $J_1$  and  $J_2$  (Fig. 6). The stronger exchange  $J_2$  forms a spin dimer for each  $\text{Fe}_2\text{O}_9$  dumbbell, and these spin dimers are antiferromagnetically coupled by the intra layer exchange  $J_1$  to form a G type AFM slab. The spin exchanges values  $J_1$  and  $J_2$  are slightly stronger but comparable for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$  than for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Se}_2$ , which is consistent with their comparable  $T_N$ . The  $\parallel ab$  spin orientations observed for  $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{Q}_2$  (Q = Se, S) are well reproduced by DFT+U+SOC calculations. From this study emerge the very comparable behaviors of isomorph layered oxy selenide and oxy sulfides. Their very close electro negativities (2.4 for Se vs. 2.5 for S), but different anionic radii (1.98 Å for  $\text{Se}^{2-}$  vs. 1.84 Å for  $\text{S}^{2-}$ ) imply different polarizing powers on the magnetic paths. It follows in such disconnected crystal structures that the effect of dipole dipole magnetic interactions beyond the through bond interactions is significant and responsible for tight Néel temperatures in these 2D structural topologies.

## Acknowledgments

This work was carried out under the framework of the ANR project ANION CO (12 JS08 0012). X Rays Diffractometers are funded by Région NPDC, FEDER, CNRS and MESR. The work at NCSU used resources of the HPC Center of NCSU and those of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U. S. Department of Energy under Contract No. DE AC02 05CH11231. National Natural Science Foundation of China (Grant No. 21671185) is gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmmm.2017.07.026>.

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