

Tetrastrontium dimanganese copper  
nonaoxide,  $\text{Sr}_4\text{Mn}_2\text{CuO}_9$ Ahmed El Abed,<sup>†</sup> Etienne Gaudin\* and Jacques DarrietICMCB, UPR9048 CNRS, Université Bordeaux 1, 87 Avenue du Docteur Schweitzer,  
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Single crystals of  $\text{Sr}_4\text{Mn}_{2.09}\text{Cu}_{0.91}\text{O}_9$  have been grown by flux synthesis and the structure, closely related to the hexagonal perovskite 2H, was solved from single-crystal X-ray data in space group  $P321$ . The structure of  $\text{Sr}_4\text{Mn}_2\text{CuO}_9$  is composed of chains of face-sharing polyhedra with a sequence of two octahedra and one trigonal prism. The octahedra are filled by Mn atoms and the Cu atoms are randomly distributed at the centres of the square faces of the trigonal prism. A stacking fault is observed within one of the two chains, which can be attributed to a shifting of the chain along the  $c$  axis.

## Comment

Numerous compounds related to the perovskite 2H, with the general formula  $A_{1+x}(A'_x B_{1-x})\text{O}_3$  (where  $0 \leq x \leq \frac{1}{2}$ ,  $A$  is an alkaline earth, and  $A'$  and  $B$  are alkali, alkaline earth or  $d$  transition elements), have been synthesized over the last few years. Their structures consist of chains of  $B^{\text{IV}}\text{O}_6$  octahedra and  $A^{\text{II}}\text{O}_6$  trigonal prisms sharing faces along the  $c$  axis, separated by  $A$  cations. One of the reasons for the interest in studying such compounds is the possibility of using various combinations of  $d$  metals on the  $A'$  and  $B$  sites to modulate magnetic properties. For example, in the case of  $\text{Sr}_4\text{Mn}_2\text{NiO}_9$  ( $x = \frac{1}{3}$ ; El Abed *et al.*, 2001, 2002), it has been shown, by means of magnetic measurements and XANES (X-ray absorption near-edge structure), that the  $\text{Mn}^{\text{IV}}$  atoms occupy the  $B$  site and the  $\text{Ni}^{\text{II}}$  atoms occupy the  $A'$  site. The global magnetic susceptibility has been described by a simple model consisting of two independent spin sub-lattices, namely anti-ferromagnetically coupled  $(\text{Mn}^{4+})_2$  dimers and paramagnetic  $\text{Ni}^{2+}$  cations at the centre of the trigonal prism. In order to verify whether this description can be extended to other compounds of this family, the title compound,  $\text{Sr}_4\text{Mn}_2\text{CuO}_9$ , has been synthesized and its structure is presented here.

The structure of  $\text{Sr}_4\text{Mn}_2\text{CuO}_9$  is composed of two different chains of face-sharing polyhedra, with a sequence of two

octahedra and one trigonal prism. One chain is centred at  $(x = 0, y = 0)$ , while the other is centred at  $(x = \frac{1}{3}, y = \frac{2}{3})$  and  $(x = \frac{2}{3}, y = \frac{1}{3})$ . The octahedra are filled by Mn atoms, and the Cu atoms are randomly distributed at the centres of the square faces of the trigonal prism. The chains are held together by Sr atoms in three different irregular ten-, nine- and eight-coordinated sites (Fig. 1).

A stacking fault is observed in the chain located at  $(x = \frac{2}{3}, y = \frac{1}{3})$ , with the occurrence of an Mn octahedron instead of a trigonal prism (Fig. 2). This stacking fault may be attributed to a shifting of the chain along the  $c$  axis. This shifting would induce the existence of disordered Cu positions around the Mn2 position. It was not possible to refine a model properly with these positions, the density being delocalized. The stacking fault density is about 14% in this chain.

Even though it is difficult to distinguish clearly between Mn and Cu by X-ray diffraction because of their similar scattering factors, several indications allow us to confirm this cationic distribution. First, from a chemical point of view, all the electron density found in the square face of the trigonal prism should correspond to  $\text{Cu}^{\text{II}}$ . Secondly, a partial substitution of Mn by Cu in the octahedra leads to a higher residual factor and non-definite positive atomic displacement parameters for some O atoms if the Cu ratio is too high. Finally, the calculations of bond-valence sums are in good agreement with the structure proposed (see below).

For the Mn1, Mn2 and Mn3 positions, the  $\text{MnO}_6$  octahedra are quite regular, with Mn—O distances close to the values previously observed in  $\text{SrMnO}_3$  (1.872 and 1.906 Å; Battle *et al.*, 1988) and reported by Shannon (1976) (1.93 Å). This is also the case for the extra Mn position Mn2p, corresponding to the stacking fault, when considering the O4 and O3b positions (Fig. 2). It is observed that the Mn2p and O3b fractional occupancies of 0.139 (7) and 0.140 (9), respectively, are very similar, as expected.

The four Cu—O distances correspond to the values found in  $\text{Sr}_3\text{CuPtO}_6$  (2.003 and 2.018 Å; Hodeau *et al.*, 1992) and are

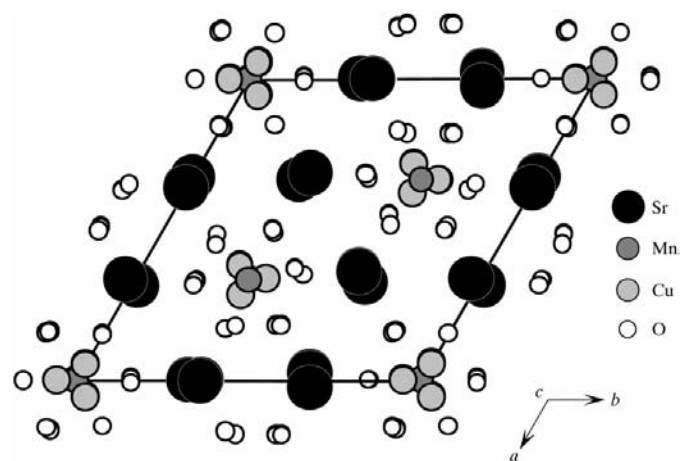
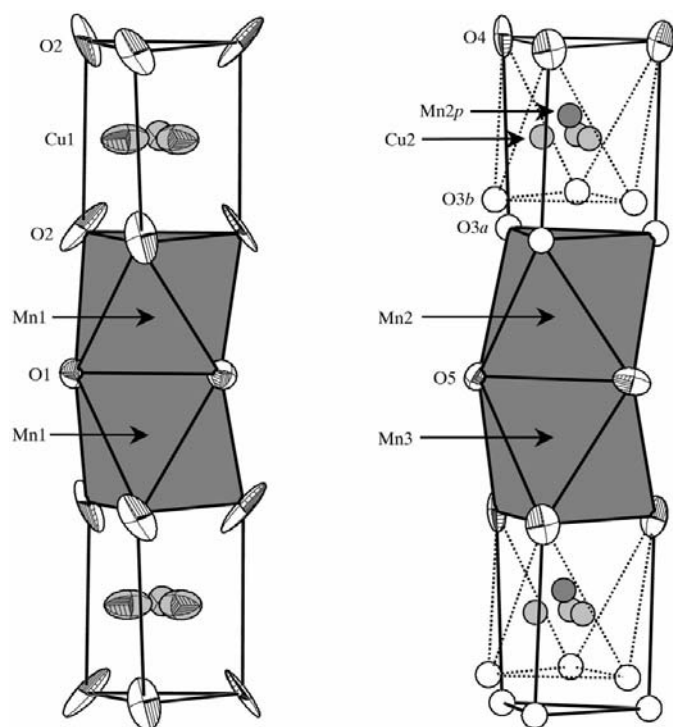


Figure 1

A view of the structure of  $\text{Sr}_4\text{Mn}_2\text{CuO}_9$  down the chain direction. The first chain is located at  $(x = 0, y = 0)$ , and the second is located at  $(x = \frac{1}{3}, y = \frac{2}{3})$  and  $(x = \frac{2}{3}, y = \frac{1}{3})$ .

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**Figure 2**  
A view of the two types of chains, at  $(x = 0, y = 0)$  (left) and  $(x = \frac{1}{3}, y = \frac{2}{3})$  (right). Displacement ellipsoids are shown at the 90% probability level and atoms which were refined isotropically are represented by spheres of arbitrary radii.

slightly greater than the value calculated according to Shannon (1996) (1.97 Å).

The short Mn–Mn distances are characteristic of Mn<sup>IV</sup> cations in face-sharing octahedra (2.500 Å in SrMnO<sub>3</sub>, for instance). However, the Mn2*p*–Mn3 distance is a little too short, and this may be attributed to the constraints introduced in the refinement between Cu2 and Mn2*p*.

The calculated bond-valence (BV) sums are 4.0, 4.3 and 3.8 for Mn1, Mn2 and Mn3, respectively, and 3.8 for Mn2*p* with O4 and O3*b* as neighbours; the values for the BV calculation are taken from Brown & Altermatt (1985). These values are in good agreement with the proposed charge balance of Sr<sub>4</sub><sup>2+</sup>Mn<sub>2</sub><sup>4+</sup>Cu<sub>2</sub><sup>2+</sup>O<sub>9</sub><sup>2-</sup>.

In the case of Cu, the calculated BV sums, considering the four Cu–O distances for both square-planar sites, are 1.4. As the contributions of the two extra Cu–O distances are significant, at around 0.1 for each bond, they should be included in the BV sum calculation, leading to a value of 1.6 for both Cu positions. The BV sums for Cu are less than 2 because the interatomic distances are constrained by the lattice structure. These internal strains can be correlated with the high atomic displacement parameters of the O atoms belonging to the trigonal prism. This oxygen motion or disorder tends to reduce the distances between the occupied Cu site and the O atoms that form the square around it (Fig. 2).

The synthesis of a pure powder sample is still in progress, in order to see if our magnetic model based on two independent sub-systems is also valid for this compound.

## Experimental

Single crystals of Sr<sub>4</sub>Mn<sub>2</sub>CuO<sub>9</sub> were grown by flux synthesis. The reagents, SrCO<sub>3</sub> (Aldrich 99.9+%), Mn<sub>2</sub>O<sub>3</sub> (Aldrich 99.999%) and CuO (Aldrich 99.99+%) (total 1.5 g), were mixed thoroughly in stoichiometric proportions and placed in an alumina crucible. K<sub>2</sub>CO<sub>3</sub> (about 20 g; Aldrich 99.99%) was added on top of the reagents. The filled crucible was covered and heated in air from room temperature to the reaction temperature of 1200 K at a rate of 60 K h<sup>-1</sup>, held at this temperature for 48 h, and subsequently cooled to 880 K at a rate of 6 K h<sup>-1</sup>. The furnace was then turned off and the system allowed to cool to room temperature. The final product was recovered from the melt by washing with distilled water.

### Crystal data

Sr<sub>4</sub>Mn<sub>2.09</sub>Cu<sub>0.91</sub>O<sub>9</sub>  
*M<sub>r</sub>* = 667.9  
 Trigonal, *P*321  
*a* = 9.5817 (2) Å  
*c* = 7.8290 (2) Å  
*V* = 622.48 (2) Å<sup>3</sup>  
*Z* = 3  
*D<sub>x</sub>* = 5.337 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 13 458 reflections  
 $\theta$  = 3.3–35.0°  
 $\mu$  = 30.90 mm<sup>-1</sup>  
*T* = 293 K  
 Block, black  
 0.09 × 0.06 × 0.03 mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 CCD scans  
 Absorption correction: Gaussian (Templeton & Templeton, 1978)  
 $T_{\min}$  = 0.164,  $T_{\max}$  = 0.468  
 11 119 measured reflections

1837 independent reflections  
 1517 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.067  
 $\theta_{\text{max}}$  = 35°  
 $h$  = -15 → 15  
 $k$  = -14 → 15  
 $l$  = -12 → 12

### Refinement

Refinement on  $F^2$   
 $R(F)$  = 0.034  
 $wR(F^2)$  = 0.076  
 $S$  = 1.04  
 1837 reflections  
 82 parameters  
 $w = 1/[\sigma^2(I) + 0.0009I^2]$

$(\Delta/\sigma)_{\text{max}}$  = 0.001  
 $\Delta\rho_{\text{max}}$  = 1.28 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -1.55 e Å<sup>-3</sup>  
 Extinction correction: Becker & Coppens (1974), type I  
 Extinction coefficient: 0.09 (2)

The common obverse/reverse twinning law was introduced. The twin matrix was (-100/0-10/001) and the refined twin ratio was 0.1169 (14). Because of this twinning, the Flack (1983) parameter was not introduced. Both absolute structures were tested and gave the same result. A model with the O2, O3 and O4 positions disordered over two sites was tested. The *R* and *wR* factors were good (0.035 and

**Table 1**  
Selected interatomic distances (Å).

Mn1–Mn1 <sup>i</sup>	2.559 (2)	Cu1–O2	2.055 (8)
Mn1–Cu1	2.6863 (16)	Cu1–O2 <sup>iv</sup>	2.582 (6)
Mn1–O1 <sup>ii</sup>	1.946 (7)	Cu1–O2 <sup>v</sup>	2.077 (9)
Mn1–O2	1.871 (8)	Cu2–O3 <i>a</i>	2.513 (10)
Mn2–Mn3	2.582 (3)	Cu2–O3 <i>a</i> <sup>vi</sup>	2.069 (10)
Mn2–Cu2	2.641 (3)	Cu2–O3 <i>a</i> <sup>vii</sup>	2.046 (7)
Mn2–O3 <i>a</i>	1.777 (9)	Cu2–O4	2.060 (6)
Mn2–O5	2.013 (5)	Cu2–O4 <sup>vi</sup>	2.082 (6)
Mn3–Cu2 <sup>iii</sup>	2.691 (3)	Cu2–O4 <sup>vii</sup>	2.545 (9)
Mn3–Mn2 <i>p</i> <sup>iii</sup>	2.292 (16)	Mn2 <i>p</i> –O3 <i>b</i>	1.90 (3)
Mn3–O4 <sup>iii</sup>	1.891 (7)	Mn2 <i>p</i> –O4	1.952 (12)
Mn3–O5	1.956 (5)		

Symmetry codes: (i)  $y, x, 1 - z$ ; (ii)  $x - 1, y, z$ ; (iii)  $x, y, z - 1$ ; (iv)  $-y, x - y, z$ ; (v)  $-x + y, -x, z$ ; (vi)  $1 - y, x - y, z$ ; (vii)  $1 - x + y, 1 - x, z$ .

0.071, respectively), but a strong correlation was observed, with large s.u. values for the O-atom occupancies. A refinement with Cu positions around the Mn2 position was also tested, but gave negative displacement parameters for some O-atom positions. Concerning the Cu disorder, no evidence of superstructure or lowering of the trigonal symmetry was observed, as in Sr<sub>3</sub>CuPtO<sub>6</sub> (Hodeau *et al.*, 1992). The total occupancies of O3a+O3b and Cu<sub>2</sub>+Mn2p were constrained to unity.

Data collection: *KappaCCD Software* (Nonius, 1999); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *JANA2000* (Petříček & Dušek, 2000); program(s) used to refine structure: *JANA2000*; software used to prepare material for publication: *JANA2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1374). Services for accessing these data are described at the back of the journal.

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