

# Magnetism and the magnetic structure of the pillared perovskite, $\text{La}_5\text{Re}_3\text{MnO}_{16}$

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We dedicate this paper to Professor Martha Greenblatt, a valued collaborator and colleague over many years

## Abstract

The new, pillared perovskite material,  $\text{La}_5\text{Re}_3\text{MnO}_{16}$ , has been synthesized by a somewhat modified method than that published previously (J. Solid State Chem. 151 (2000) 31) in sufficient quantities for neutron diffraction experiments. Such experiments were carried out between 10 and 250 K at zero applied field. The crystal structure found at 250 K from refinement of powder neutron diffraction data is in excellent agreement with previous results obtained from a single crystal X-ray experiment. Bulk susceptibility measurements show a sharp spike at 161 K and a broad maximum at  $\sim 100$  K. Long range magnetic order was found below the critical temperature of  $\sim 165$  K with an ordering wave vector,  $\mathbf{k} = (00 \frac{1}{2})$ . The magnetic structure found consists of perovskite type layers containing  $\text{Re}^{5+}$  and  $\text{Mn}^{2+}$  moments coupled ferrimagnetically (Re antiparallel to Mn) within the layers and with antiferromagnetic interlayer coupling. The ordered moments at 10 K are  $4.0(1)\mu_B$  for  $\text{Mn}^{2+}$  and  $1.0(1)\mu_B$  for  $\text{Re}^{5+}$ , not unreasonable values. The Re moments lie nearly along the  $c$ -axis while the Mn moments make an angle of  $\sim 18^\circ$  with respect to  $c$ . While most of the magnetic scattering can be accounted for by the above model, two weak reflections are seen which appear at 90 K and below and require  $\mathbf{k} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$ . © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

## 1. Introduction

Recently, a new structure type has been found which can be described as a pillared perovskite. Two known examples are the oxides,  $\text{La}_5\text{Mo}_4\text{O}_{16}$  and  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  [1,2]. The structure type can be described in general terms as  $\text{Ln}_5\text{M}_2\text{ABO}_{16}$ , where layers of composition  $\text{ABO}_6$ , consisting of corner-sharing metal–oxygen octahedra with site-ordering between A and B, are connected by  $\text{M}_2\text{O}_{10}$  dimeric units, consisting of edge-sharing metal–oxygen octahedra, orientated normal to the  $\text{ABO}_6$  layers, i.e., pillaring the layers. The  $\text{Ln}^{3+}$  ions occupy the interstices between the layers and the dimers. A view of the structure illustrated by the  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  compound is shown in Fig. 1. Note that the dimeric units connect directly only one type of atom, B, between layers. An exploration of the crystal chemistry of the family  $\text{La}_5\text{Re}_2\text{ReMnO}_{16}$  has

been carried out in which various divalent B ions have been substituted for  $\text{Mn}^{2+}$  (the oxidation state of Re is 5+) which will be described in a separate publication. Relatively little is known about the physical properties of these materials which present a new type of layered structure and contain magnetic ions from both the well studied 3d transition series and the less familiar 4d and 5d series. Magnetic measurements indicate rather high transition temperatures of  $\sim 200$  K for the Mo phase [3] and  $\sim 160$  K for the ReMn phase which is surprising given that the dimeric coupling units are diamagnetic, containing M–M double bonds and the interlayer separation is  $\sim 10$  Å. The appearance of the magnetic transition is unusual, consisting of a sharp spike in the susceptibility followed at lower temperature by some evidence for a divergence in the field-cooled, zero-field-cooled curves [2]. For the ReMn compound, fits of the susceptibility to a Curie–Weiss law give a  $\theta_c = -48$  K, indicating dominant antiferromagnetic interactions but magnetization versus field curves show a complex behavior suggesting a complicated magnetic structure. In this study we carried out neutron diffraction experiments in order to determine the magnetic structure at zero applied field. This required the development of a new synthetic

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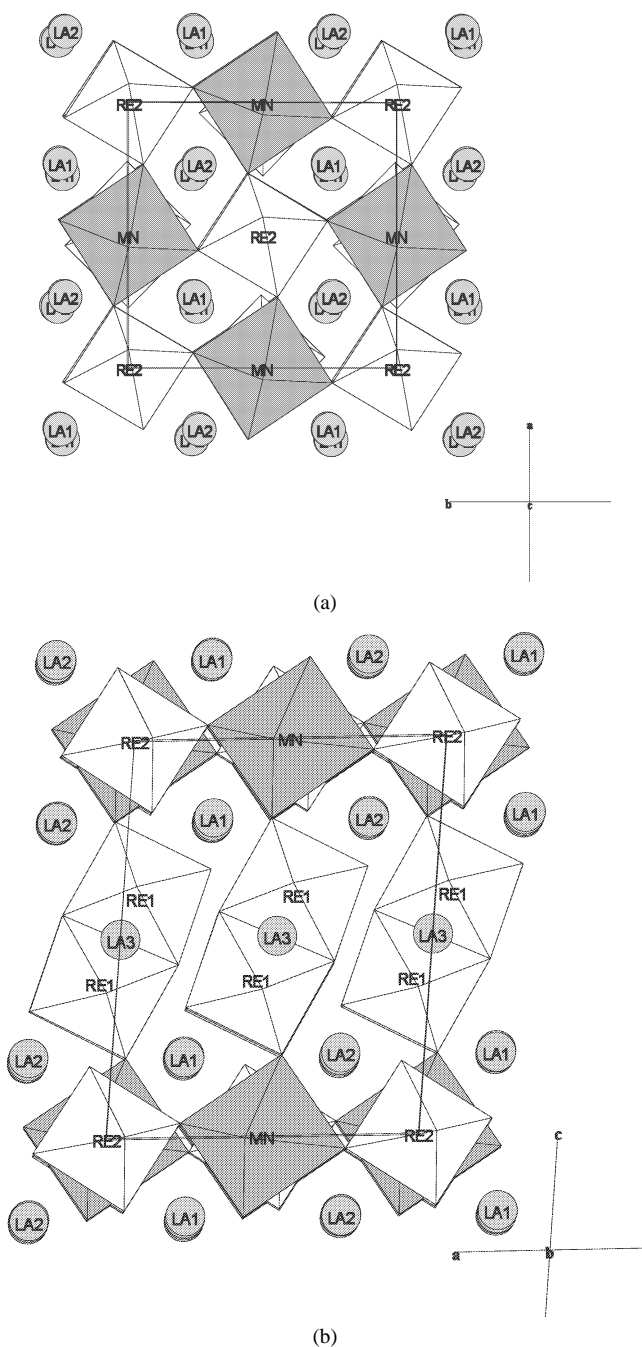


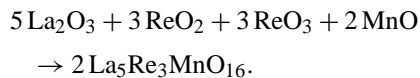
Fig. 1. The crystal structure of  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  viewed normal to the  $ab$  plane (a) and normal to the  $ac$  plane (b).

procedure as previous methods had resulted in small yields, side reactions and multi-phase products [2].

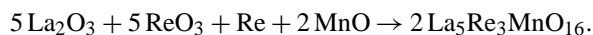
## 2. Experimental

### 2.1. Sample preparation

Previous efforts to prepare  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  involved the reaction sequence below:



This resulted in a two-phase product consisting of a transparent glassy phase surrounding a core of the desired product [2]. It was found that a single phase product could be obtained from the following solid state reaction:



Stoichiometric quantities of the above reagents were ground in an agate mortar and pestle to produce a homogenous mixture. Pellets were pressed and placed into a platinum capsule which was then sealed into a quartz tube under a vacuum of  $\sim 10^{-5}$  Torr. This vessel was placed in a tube furnace and heated twice at  $1050^\circ\text{C}$  for 48 h with a regrinding step between firings. The yields from the above were essentially quantitative, allowing the preparation of several grams for neutron diffraction experiments.

### 2.2. X-ray diffraction

X-ray diffraction data were obtained with a Guinier–Hägg camera with  $\text{Cu } K_{\alpha 1}$  radiation of wavelength  $\lambda = 1.54056 \text{ \AA}$ . High purity silicon powder was used as an internal standard. A KEJ Instruments LS-20 line scanner was used to scan the film and convert the data to a digital file. The data were analyzed using the programs SCANPI and LSUDF. The unit cell parameters were obtained using a starting model based on the known single crystal structural data [2].

### 2.3. Neutron diffraction

Powder neutron diffraction data were collected using the C2 diffractometer which is operated by the Neutron Program for Materials Research of the National Research Council of Canada at the Chalk River Nuclear Laboratories. The neutron wavelength was  $\lambda = 2.3688 \text{ \AA}$  and data were obtained over the angular range  $5 < 2\theta < 114.9^\circ$ , with a step width of  $0.1^\circ$  at several temperatures from 10 to 250 K. The sample consisted of about 3 g of powder contained in a vanadium can sealed under helium exchange gas.

The data were analyzed using the program FULLPROF 3.5d Rietveld refinement package. The program BONDS was used to calculate bond distances and angles.

### 2.4. Magnetic measurements

Measurements of the magnetic properties were made using a MPMS SQUID magnetometer from Quantum Design. Data were collected as a function of temperature in both zero-field-cooled (ZFC) and field-cooled (FC) modes over the range 5–350 K at an applied field of 500 Oe. As well, isothermal field sweeps were carried out over the range 0–2.5 T at 5, 75, 145 and 250 K.

Table 1

Positional parameters refined from powder neutron diffraction data for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  for 10 and 250 K

	$x$ (10 K)	$y$ (10 K)	$z$ (10 K)	$x$ (250 K)	$y$ (250 K)	$z$ (250 K)	$B$ ( $\text{\AA}^2$ )
La1	0.230(2)	0.740(2)	0.797(2)	0.227(1)	0.743(1)	0.799(1)	0.78(24)
La2	0.227(2)	0.263(2)	0.793(2)	0.228(1)	0.282(2)	0.789(1)	0.78(24)
La3	0.5	0.5	0.5	0.5	0.5	0.5	0.78(24)
Re1	0.053(1)	0.494(2)	0.392(1)	0.053(1)	0.496(1)	0.393(1)	0.38(16)
Re2	0	0	0	0	0	0	0.38(16)
Mn	0	0.5	0	0	0.5	0	0.51(20)
O1	0.189(2)	0.504(4)	0.565(2)	0.189(2)	0.508(3)	0.564(1)	0.76(54)
O2	0.276(2)	0.497(4)	0.316(2)	0.275(1)	0.493(2)	0.320(1)	0.76(54)
O3	−0.042(2)	0.503(4)	0.196(1)	−0.042(1)	0.500(2)	0.200(1)	0.76(54)
O4	0.072(2)	−0.015(3)	0.181(2)	0.073(2)	−0.011(2)	0.179(1)	0.76(54)
O5	0.034(2)	0.734(4)	0.366(3)	0.034(2)	0.733(2)	0.363(1)	0.76(54)
O6	0.038(3)	0.261(4)	0.367(3)	0.036(2)	0.264(2)	0.371(2)	0.76(54)
O7	−0.058(2)	0.249(3)	0.001(2)	−0.059(1)	0.244(2)	0.004(1)	0.76(54)
O8	0.240(2)	0.062(2)	−0.026(2)	0.238(2)	0.059(1)	−0.028(1)	0.76(54)

Table 2

Cell parameters, magnetic moments and agreement indices for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  for 10 and 250 K

	10 K	250 K
Mn moment ( $\mu_B$ )	3.9(1)	0
Re moment ( $\mu_B$ )	1.0(1)	0
$a$ ( $\text{\AA}$ )	7.9660(5)	7.9836(4)
$b$ ( $\text{\AA}$ )	8.0084(5)	8.0208(3)
$c$ ( $\text{\AA}$ )	10.2095(7)	10.2269(5)
$\alpha$ (deg)	90.185(6)	90.181(4)
$\beta$ (deg)	95.193(4)	95.182(3)
$\gamma$ (deg)	89.933(6)	89.944(5)
Volume ( $\text{\AA}^3$ )	648.65(7)	652.20(5)
$R_p$	5.16	4.55
$R_{wp}$	6.77	6.30
$R_{exp}$	2.53	2.68
$\chi^2$	7.14	5.53
Bragg $R$ -factor	5.03	5.20
$R - F$	3.70	3.88
Magnetic $R$ -factor	22.7	–

### 3. Results and discussion

#### 3.1. X-ray diffraction

The Guinier–Hågg camera data consisted of 41 lines. It was possible to index all of the observed reflections using a triclinic cell of symmetry  $C-1$  with the cell constants

$$a = 7.988(1) [7.984(7)], \quad b = 8.053(3) [8.020(3)],$$

$$c = 10.215(2) [10.255(8)],$$

$$\alpha = 90.14(2)^\circ [90.19(4)^\circ], \quad \beta = 95.18(2)^\circ [95.29(3)^\circ],$$

$$\gamma = 89.89(3)^\circ [90.17(4)^\circ].$$

The values in square brackets are those from the single crystal experiment and the agreement is seen to be reasonable [2]. Thus, it appears that the new synthetic method has yielded single phase  $\text{La}_5\text{Re}_3\text{MnO}_{16}$ .

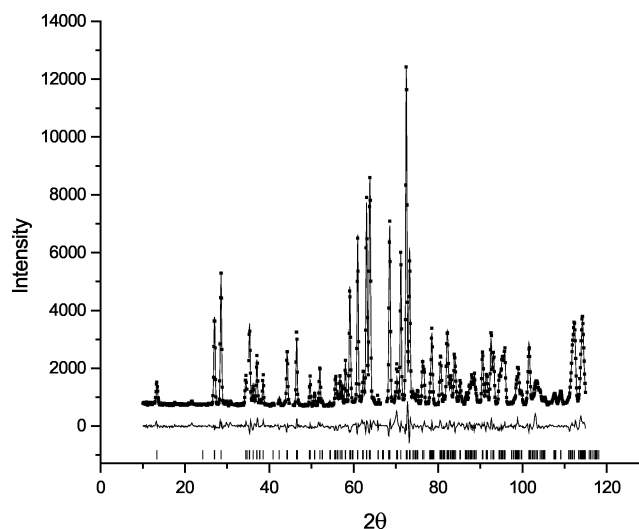


Fig. 2. Rietveld refinement of the 250 K neutron diffraction data for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$ . The filled circles represent the data, the solid line is the fit and the difference is shown below. The tick marks show the Bragg peak positions.

#### 3.2. Crystal structure

A refinement of the neutron diffraction data at 250 K is shown in Fig. 2 and the results are tabulated in Tables 1 and 2. The single crystal refinement parameter values were used as the starting model. Although the powder data set is limited by the long wavelength and the instrument geometry, which permits a maximum scattering angle of only  $\sim 115^\circ$  ( $2\theta$ ), the agreement between the powder neutron and single crystal X-ray refinement results [2] is good and provides further confidence that the powder and single crystal samples are not essentially different.

#### 3.3. Magnetic properties

Fig. 3 shows the measured susceptibility data for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  over the temperature range 5 to 350 K. These results are consistent with those published previously [2]

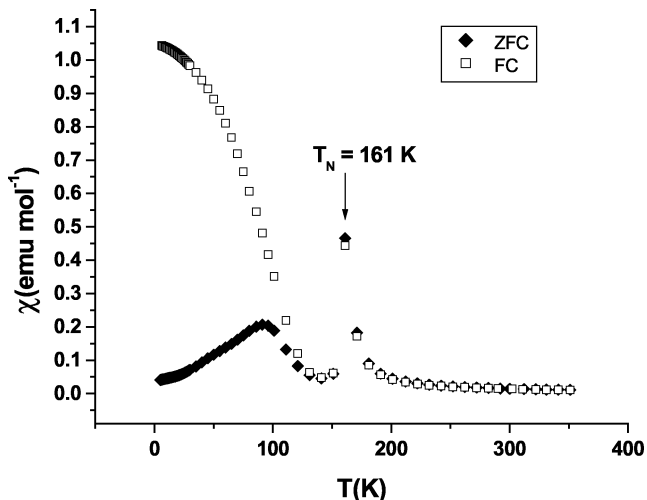


Fig. 3. The magnetic susceptibility versus temperature for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  for both field-cooled (FC) and zero-field-cooled (ZFC) modes.

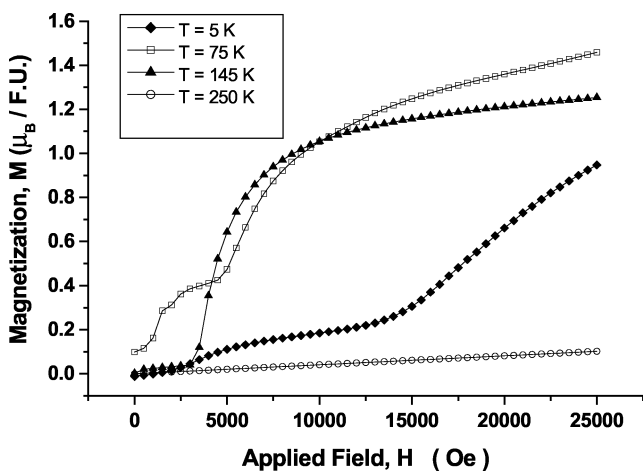


Fig. 4. The magnetization versus applied field at selected temperatures for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$ .

in that a sharp spike is seen at  $\sim 160$  K but there is an additional, pronounced, broad maximum at  $\sim 90$  K and ZFC–FC divergence sets in below 125 K. These details differ slightly from the previous report where the low temperature maximum was much weaker and centered at about  $\sim 60$  K with the ZFC–FC divergence occurring below 100 K. This suggests a slight sample to sample dependence for these secondary magnetic properties. The isothermal field sweeps are shown in Fig. 4 and are also similar to those seen before but in this case more temperatures are investigated. The result for 250 K, well above the apparent ordering temperature of 160 K, shows a typical paramagnetic response, i.e., a constant  $M/H$  ratio at all fields. For the three temperatures below  $T_c$  sharp jumps in the magnetization at rather low fields, between 0.3 and 0.4 T, are apparent, behavior not unusual for layered magnetic materials which may signal a metamagnetic transition.

The data for 75 K also show a weak anomaly at an even lower field of 0.1 T and the 5 K data show a more grad-

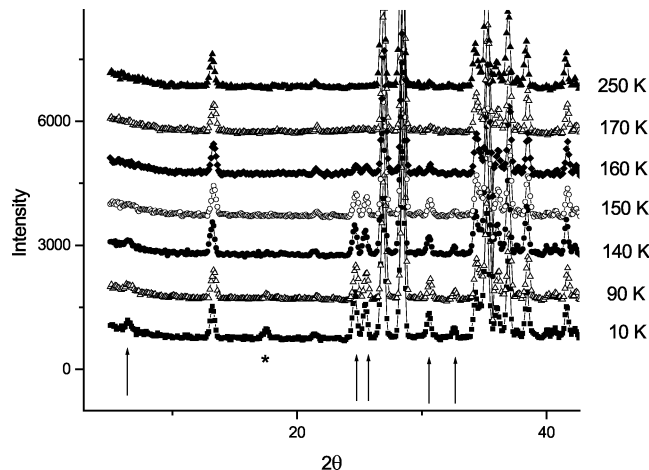


Fig. 5. Low angle neutron diffraction data for  $\text{La}_5\text{Re}_3\text{MnO}_{16}$  at selected temperatures showing the development of new reflections below 160 K. The magnetic reflections belonging to  $\mathbf{k} = (00\frac{1}{2})$  are marked by arrows and the reflection belonging to  $\mathbf{k} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$  is marked by a star (\*).

ual jump at 1.5 T. The observation of metamagnetic-like anomalies at such low fields is an indication of weak interplanar exchange as might be expected. That the magnetization is small and nearly linear in field at low fields for the 5 K data indicates that the ground state magnetic structure at zero field involves both intra and inter layer antiferromagnetic couplings. This might be at first glance surprising as two magnetic species with quite different magnetic moments are involved,  $\text{Re}^{5+}$ ,  $5d^2$ ,  $S = 1$ , and  $\text{Mn}^{2+}$ ,  $3d^5$ ,  $S = 5/2$ . Furthermore, the Goodenough–Kanamori rules predict weak ferromagnetic exchange coupling for  $d^2$ – $d^5$  superexchange which obtains within the layers [4]. Nonetheless, it is important to recall that these rules assume ideal  $180^\circ$  Re–O–Mn bond geometry and the actual bond angles are much more acute at  $\sim 148^\circ$  and  $154^\circ$ , so the orthogonality conditions which pertain at  $180^\circ$  must be heavily modified in the real material. Antiferromagnetic  $d^2$ – $d^5$  superexchange is more consistent with the observed negative Curie–Weiss theta value of  $\sim -50$  K.

### 3.4. Magnetic structure

As seen in Fig. 5, several new reflections develop at 10 K. The strongest of these can be indexed on a magnetic cell with dimensions  $a_{\text{mag}} = a$ ,  $b_{\text{mag}} = b$  and  $c_{\text{mag}} = 2c$  with respect to the chemical cell, i.e., with an ordering wave vector  $\mathbf{k} = (00\frac{1}{2})$ . Fig. 6 shows the temperature dependence of the four strongest reflections. Clearly, the temperature dependence is consistent with an ordering temperature of  $\approx 162$  K, in accord with the susceptibility data. Also included in Fig. 6 is a weak reflection which requires a different ordering wave vector,  $\mathbf{k} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ , and which clearly has a different temperature dependence. This feature and another with the same temperature dependence which is severely overlapped by structure peaks at higher angles were excluded from the refinements of the magnetic structure defined by the strong

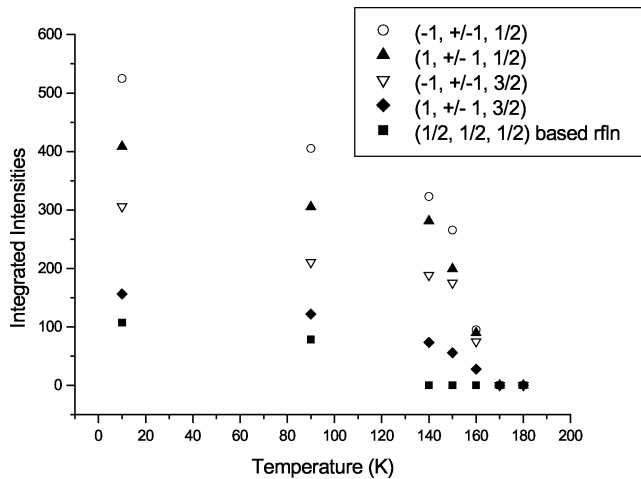


Fig. 6. The temperature dependence of the strongest magnetic reflections belonging to the  $\mathbf{k} = (00\frac{1}{2})$  magnetic structure along with an additional weak reflection indexed with  $\mathbf{k} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ .

reflections. These reflections may be associated with the susceptibility anomaly below 100 K but it is difficult to make a definitive correlation without more diffraction data.

With an ordering wave vector of  $(00\frac{1}{2})$  a natural choice for a trial magnetic structure is one analogous to the so-called A-type structure in perovskites, where planes of ferromagnetically coupled  $ab$  layers are coupled antiferromagnetically with respect to the  $c$ -axis which would account for the doubling of the  $c$ -axis in the magnetic cell. In this case the intraplanar coupling between the different Mn and Re moments could be in principle ferromagnetic or antiferromagnetic and both models were tried. The absence of magnetic reflections of the type  $(00l)$ , except for a very weak  $(002)$  peak, indicates that the net moment direction is roughly parallel to the  $c$ -axis.

For the 10 K data set a model in which the Re moments were antiparallel to the Mn moments within the layers and with the layers coupled antiparallel was tried with initial moment values of  $4.5\mu_B$  on  $Mn^{2+}$  and  $1.5\mu_B$  on  $Re^{5+}$  (i.e., nearly the spin only values) and the direction parallel to the  $c$ -axis. The moment values were refined with the aid of soft constraints to  $3.9(1)\mu_B$  on Mn and  $1.0(1)\mu_B$  on Re, not unreasonable values. Initial models in which the intraplanar Re–Mn coupling was ferromagnetic, refined rapidly to antiparallel alignments. The orientation of the Re and Mn moments with respect to the  $c$ -axis was also refined, given the presence of a weak  $(002)$  peak and slightly different angles were obtained, with the Re moments nearly parallel to  $c$  and the Mn moments aligning  $\sim 18^\circ$  with respect to  $c$ . The results of the combined chemical structure/magnetic structure refinements are listed in Tables 1 and 2 for the 10 K data and the data refinement for 10 K is shown in Fig. 7. Fig. 8 displays the magnetic structure associated with the  $\mathbf{k} = (00\frac{1}{2})$  wave vector.

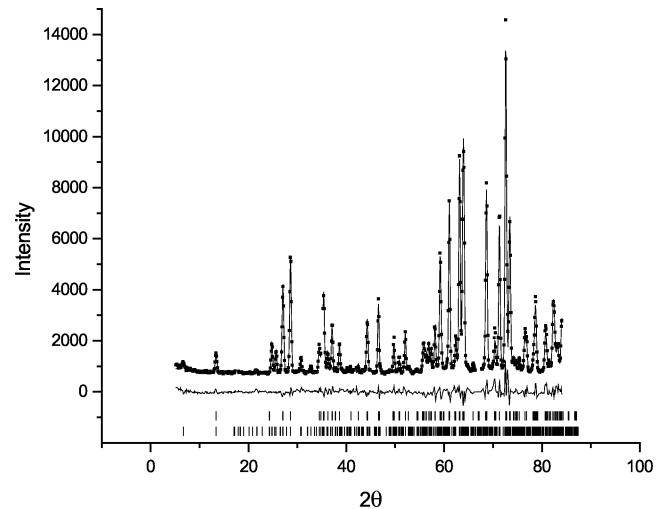


Fig. 7. Simultaneous crystal structure/magnetic structure Rietveld refinement of the 10 K data for  $La_5Re_3MnO_{16}$ . The filled circles are the data, the solid line is the fit, the difference plot is shown below and the crystal structure reflections (top) and the magnetic structure reflections (bottom) are marked.

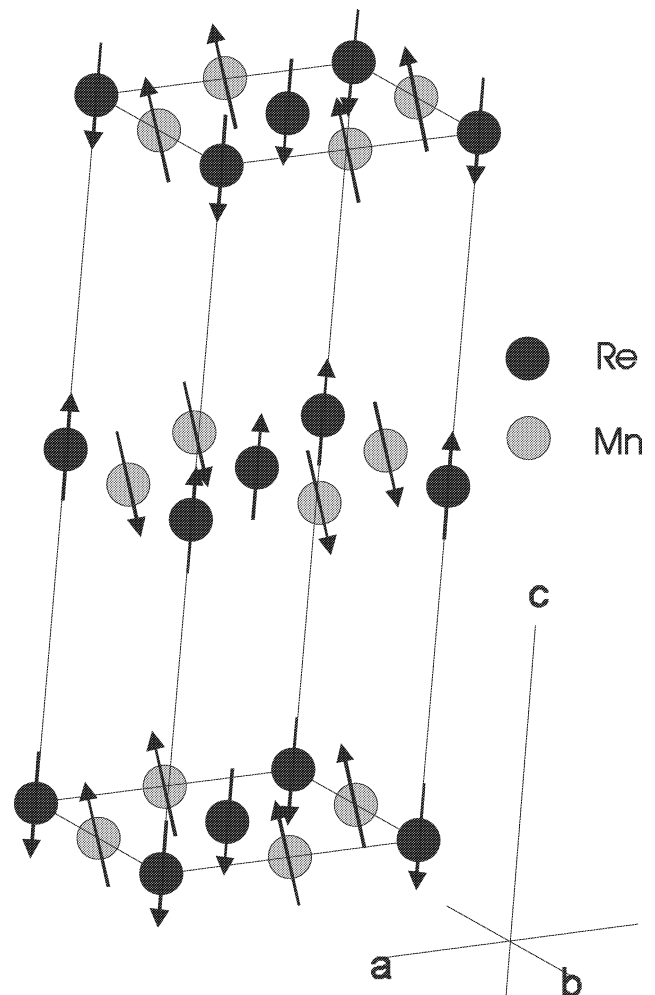


Fig. 8. The refined magnetic structure for  $La_5Re_3MnO_{16}$ .

#### 4. Summary

The bulk magnetic properties and the magnetic structure of the pillared perovskite,  $\text{La}_5\text{Re}_3\text{MnO}_{16}$ , have been determined on polycrystalline samples. This material exhibits long range magnetic order below  $\sim 162$  K. There is evidence for metamagnetic-like transitions at low critical fields of 0.3 to 0.4 T, suggesting weak interplanar exchange couplings as would be expected from the crystal structure. The magnetic structure described by wave vector  $\mathbf{k} = (00\frac{1}{2})$  consists of layers of ferromagnetically coupled  $\text{Re}^{5+}$  and  $\text{Mn}^{2+}$  moments which are in turn coupled antiparallel along the  $c$ -axis, perpendicular to the layers. The refined moments for  $\text{Mn}^{2+}$  are slightly below the Hund's rule values,  $3.9(1)\mu_{\text{B}}$  for  $\text{Mn}^{2+}$  and  $1.0(1)\mu_{\text{B}}$  for  $\text{Re}^{5+}$  and the moment direction of the Re sublattice is nearly parallel to  $c$  while that for the Mn sublattice is  $\sim 18^\circ$  from  $c$ . The observation of two very weak reflections which appear only at 90 K and below and require a  $\mathbf{k} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$  wave vector, signals a subtle change in magnetic structure at low temperature which may be associated with the low temperature features in the bulk susceptibility.

#### Acknowledgements

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