Experimental report

13/05/2022

Proposal: **5-31-2788** **Council:** 4/2020

Title: Magnetic structure of Ca3Mn2-xRuxO7 Ruddlesden-Popper phases.

Research area: Materials

This proposal is a new proposal

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Samples: Ca3Mn2-xRuxO7 (x=0.1, 0.2, 0.3, 0.4, 0.5)
Ca3Mn1.95Ru0.05O7

Instrument	Requested days	Allocated days	From	To
D1B	3	2	01/02/2021	03/02/2021

Abstract:

We pretend to carry out a thorough magnetic study of a new set of doped manganites belonging to the Ruddlesden-Popper A3B2O7 phases. The parent compound, Ca3Mn2O7, is a promising magnetoelectric multiferroic compound. The replacement of Mn by Ru enhances the occurrence of spontaneous magnetization preserving the orthorhombic structure of Ca3Mn2O7. We expect to determine the evolution of the magnetic structure along the Ca3Mn2-xRuxO7 series up to x=0.5. Two possibilities are contemplated; on the one side, the addition of Ru can increase the canting of magnetic moments enhancing the FM component along the y-axis, hardly noticeable in the undoped compound. On the other side, Ru moments could align in opposite direction to Mn moments as observed in the simple perovskites CaMn1-xRuxO3. Neutron thermodiffractograms collected at D1B between 2 and 275 K can help to solve the magnetic structure, to discern any sort of Mn/Ru ordering and to account for the presence of short magnetic correlations above the magnetic transition in form of diffuse scattering as reported for Ca3Mn2O7.

Magnetic structure of $Ca_3Mn_{2-x}Ru_xO_7$ Ruddlesden Popper phases.

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Polycrystalline $Ca_3Mn_{2-x}Ru_xO_7$ (x=0.05, 0.1, 0.3, 0.5, 0.7, 0.9) samples were prepared by solid state reaction of Mn_2O_3, $CaCO_3$ and RuO_2 powders. Powder neutron diffraction measurements were performed at the high intensity powder diffractometer D1B (λ=2.52 Å) with a detector angular range coverage $5^o \leq 2\theta \leq 128^o$. Diffraction patterns were collected between 2 K and well above the magnetic transition temperature previously determined by macroscopic magnetic measurements. The patterns were analyzed by the Rietveld method using the Fullprof program [1]. The parent compound, $Ca_3Mn_2O_7$, undergo an antiferromagnetic (AFM) ordering of G-type at T_N=112 K [2]. Its crystal structure is orthorhombic with space group *Bb2₁m* (No. 36, standard setting *Cmc2₁*).

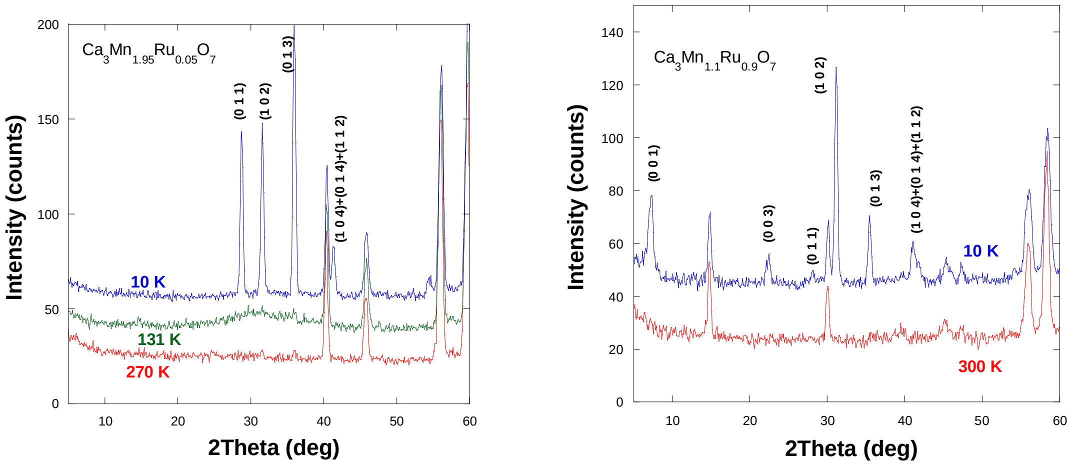

Fig. 1. *Comparison of the neutron patterns collected at different temperatures for (left) $Ca_3Mn_{1.95}Ru_{0.05}O_7$ and (right) $Ca_3Mn_{1.1}Ru_{0.9}O_7$. The patterns have been shifted upward for clarity. Indexation corresponds to the main magnetic peaks.*

The analysis of the neutron patterns at high temperature reveals that all $Ca_3Mn_{2-x}Ru_xO_7$ samples studied in this experiment adopt the same orthorhombic structure. An expansion of the unit cell volume with increasing the Ru content in the chemical composition is observed. This effect should be ascribed to the difference in ionic radii between Mn^{4+} and Ru^{4+} [3]. More significant differences are observed in the neutron patterns collected at low temperature as can be seen in Fig. 1. For low doping rates (x≤0.1), magnetic peaks can be associated to a G-type magnetic structure as observed for the undoped compound. However, an additional contribution is observed for the samples with x≥0.3. (0 0 odd) magnetic peaks are clearly noticeable indicating an A-type magnetic arrangement. The intensity of the A-type peaks increases with increasing the Ru content. In addition, diffuse magnetic scattering is observed in the patterns at temperatures above T_N suggesting the onset of short range magnetic correlations before the development of the long-range order.

A symmetry analysis disclosed the possible magnetic structures compatible with our results. Using the Bertaut's notation [4], they correspond to G_xG_y and A_xG_y structures for x≤0.1 and x≥0.3 samples, respectively. Fig. 2 shows some typical refinements and the deduced magnetic structure.

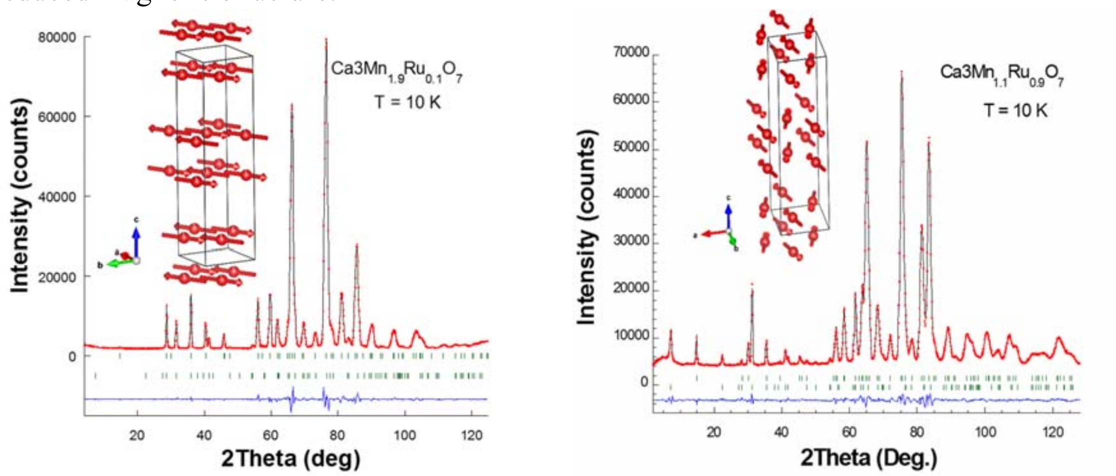

Fig. 2. *Rietveld refinement of the neutron patterns collected a 10 K for (left) $Ca_3Mn_{1.9}Ru_{0.1}O_7$ and (right) $Ca_3Mn_{1.1}Ru_{0.9}O_7$. The insets show the corresponding magnetic structures.*

Finally, this study has allowed us to outline a magnetic phase diagram of this series and to characterize the anisotropic behavior in the evolution of the lattice parameters as a function of the Ru content, as can be seen in Figure 3. Coupled to the change in the magnetic structure, changes in the c-axis trend and in the relative values of the a- and b-axes are observed.

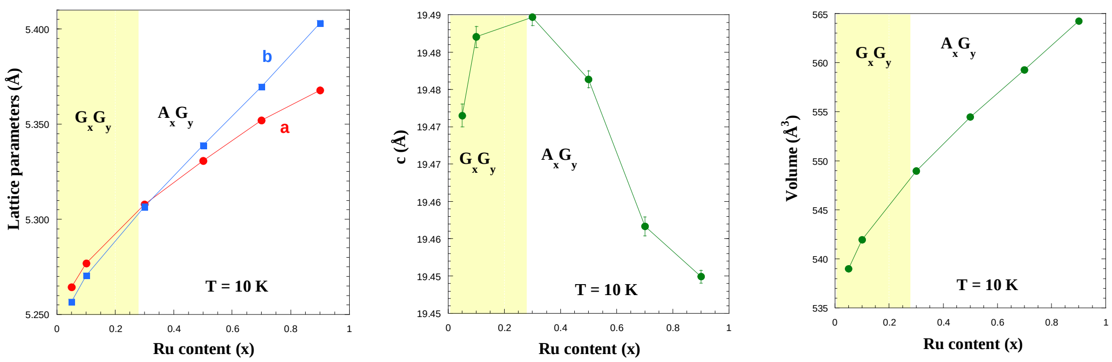

Fig. 3. *Evolution of a- and b-axes (left), c-axis (middle) and unit cell volume (right) as a function of Ru content for the $Ca_3Mn_{2-x}Ru_xO_7$ series at 10 K.*

References.

[1] J. Rodríguez-Carvajal, Physica B **192** 55 (1993).
[2] O. V. Dolomanov et al., J. Appl. Cryst. **42**, 339 (2009).
[3] R. D. Shannon, Acta Cryst. Sect A**32**, 751 (1976).
[4] E. F. Bertaut, Acta Crystallogr. Sect. A **24** 2177 (1968).