Experimental report

11/04/2016

Proposal:	**5-41-811**		**Council:**	10/2014

Title: Study of the low temperature nuclear and magnetic structure of the novel multiferroic LaMn3Mn4O12

Research area: Physics

This proposal is a new proposal

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Samples: LaMn3Mn4O12

Instrument	Requested days	Allocated days	From	To
D10	7	7	26/06/2015	03/07/2015

Abstract:

We propose a single crystal neutron diffraction study of the nuclear and magnetic structure of the quadruple perovskite (LaMn3)Mn4O12. Our motivation is a very recent observation of ferroelectricity with a polarisation P ~ 1 uC/cm2 induced by a magnetic order, to the best of our knowledge the largest value hitherto reported for an improper ferroelectric. This prompts us to investigate (i) the magnetic structure and (ii) the expected breaking of the centre of symmetry at the magnetic ordering transition. This shall enable us to elucidate the role of the exchange striction driving the ferroelectricity and stimulate the search for novel multiferroics with optimised properties.

Experimental report of proposal 5-41-811:

Study of the low temperature nuclear and magnetic structure of the novel multiferroic $(LaMn_3)Mn_4O_{12}$

Objective and expected results: The aim of the experiment was to determine the nuclear and magnetic structures of $(LaMn_3)Mn_4O_{12}$ below $T_{N,B}$ an $T_{N,A'}$ by performing neutron diffraction on single-crystal. The motivation is the possible influence of this magnetic structure on the occurence of ferroelectricity below $T_{N,B}$. The observation of ferroelectricity suggests a centre of symmetry breaking of the pseudocubic *I2/m* structure at $T_{N,B}$. Specifically, we wanted to precisely determine the magnetic structure including the canted component of the magnetic moments (Mn^{3+}) on B-sites. Although this canting seems to be evident from magnetization measurements which highlights weak ferromagnetism at $T_{N,B}$ (cf A.Prodi *et al.*,PRB, **79**, 085105) it was not been evidenced by previous neutron diffraction on powder sample and it could constitute an explanation for the occurence of ferroelectricity. Indeed, by symmetry, the C-type magnetic structure is not compatible with a centre of symmetry breaking, whilst a canted structure may lead to spin-induced ferroelectricity via the inverse Dzyaloshinskii-Moriya effect. Another possibility is that the magnetic structure is more complex than the simple C-type previously reported and another propagation vector is present. The new data will also help to determine the magnetic structure of the Mn^{3+} A' sublattice that orders at lower temperature, $T_{N,A'}$=22 K [8].

Mesures performed during the experiment: We were able to orient a single-crystal of $\sim$500 $\times$ 1000 μm and obtained the μb matrix. This preliminary part was a challenge because of the very small size of the sample an its success paves the way to neutron diffraction experiments on small single crystal. We performed long spectra acquisition with a monitor reference of 3.000.000 or 2.500.000 which corresponded to times acquisition of 2$\sim$3 hours/ spectrum.

We measured the signal for several (hkl) positions at high temperature (100K) in the paramagnetic phase, at intermediate temperature (50K) where only B sites are oriented, and at low temperature where both A' and B sites are oriented. 100K: (110), (211), (220); 50 K: (110),(211), (220), (100), (201), (10-1); 2K: (0-10), (100), (001), (201), (-10-2), (111), (1-11), (0.63, -0.085, -0.5), (0.4, -0.915, 0.5)

As expected the magnetic peaks corresponding to B-sites (cf fig.1) are also nuclear and we can identify a strong magnetic contribution for (110) and (211) reflexions. All 3 spectra present 3 separated peaks that we interpret as domains in the crystal. Indeed, we expected to find twined domains with close orientation because of the high pressure synthesis conditions and the number is coherent with the 3 possibilities of choosing the angle of the monoclinic distorsion.

On the other hand, the magnetic peaks corresponding to A'-sites (cf fig.2) are not nuclear. In the spectrum corresponding to the (100) reflexion (left panel of fig.2) we could identify 3 peaks even if less separated than in the case of B-sites, whereas for the (201) reflexion (right panel of fig.2) there is only one peak. The data analysis in progress is expected to explain why only one domains contributes to this reflexion.

We also measured other reflexions that were not observed in the powder experiment. We first measured at 50 K the reflexion (10-1) (cf left panel of fig.3). In the hypothesis of *I2'/m'* magnetic point group which was previously proposed form powder data, this peaks is sensitive to the non-compensation of the B-spins in the ac-plan. This is very important because, in the powder data analysis, the refinement was performed using the hypothesis of spin orientation along the ac-diagonal, which seems to be an oversimplification in the light of the present single-crystal data. We were also able to measure a signal on the (1-11) reflexion (cf right panel of fig.3) at 2K which was not observed in the powder experiment. We think that this will permit to determine more precisely the magnetic structure.

Conclusion

The experiment was successful because we were able to measure all the expected magnetic reflexions at low temperature despite of the small size of the crystal and new peaks were detected. From the shape of the spectra we conclude that the crystal is composed of 3 domains whith close orientations. The ongoing data analysis shall permit to identify a μb matrix for each domain. We were also able to measure additional magnetic reflexions not observed in previous powder data. We think this will permit to precisely resolve the magnetic structure at low temperature. For example, a preliminary analysis indicates that the orientation of the B-spins is tilted with respect to the ac-diagonal and that it has a b-component. This is in contradiction with previous conclusion from powder data. We also checked the possibility of an incommensurate magnetic order as it is present in the related compound $(CaMn_3)Mn_4O_{12}$, but this is inconsistent with the observation of zero intensity of the (0.63, -0.085, -0.5) and (0.4, -0.915, 0.5) peaks. Further analysis will be performed soon and we expect to establish an accurate model of the magnetic structure that should help to understand the microscopic mechanism of the magnetically induced ferroelectricity in $(LaMn_3)Mn_4O_{12}$.

Participants: Andrea Gauzzi (main proposer); Marine Verseils (co-proposer) and Laurent Chapon (local contact).

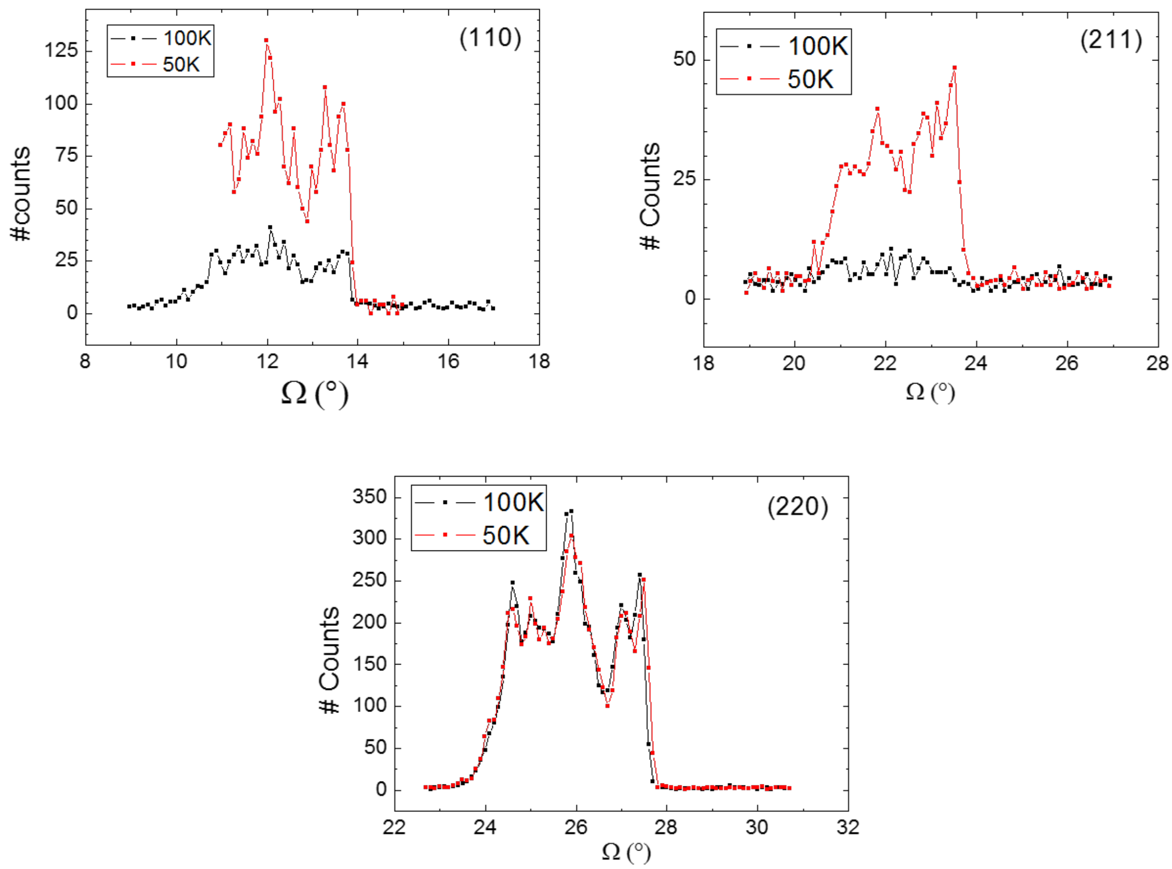

Figure 1: Spectra of the 3 magnetic peaks corresponding to sites B in the disordered phase (100K, black) and in the B-ordered phase (50K, red).

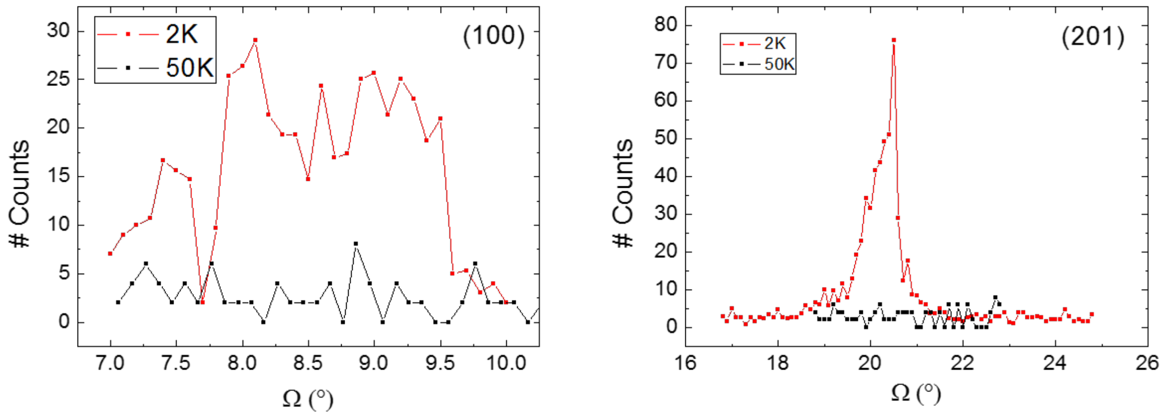

Figure 2: Spectra of the 2 magnetic peaks corresponding to sites A' in the disordered phase (50K, black) and in the A'-ordered phase (2K, red).

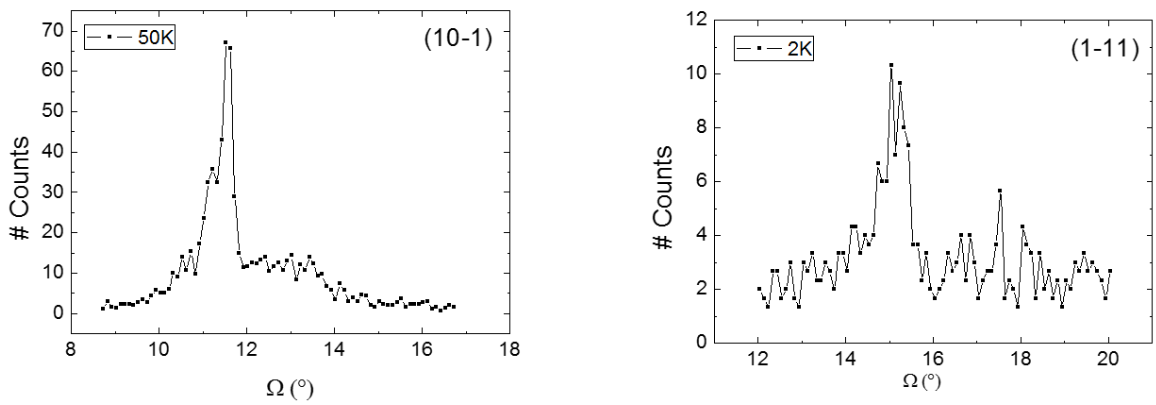

Figure 3: Left: (10-1) reflexion at T=50K. Right: (1-11) reflexion at T=2K.