Experimental report

09/02/2016

Proposal: 5-23-669 **Council:** 10/2014

Title: Investigating the temperature evolution of EuTiO3 local structure by means of Pair Distribution FunctionAnalysis

Research area: Materials

This proposal is a resubmission of 6-06-454

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Samples: EuTiO3

Instrument	Requested days	Allocated days	From	To
D4	5	5	17/07/2015	22/07/2015

Abstract:

Magnetoelectric EuTiO3 undergoes a long range cubic to tetragonal phase transition at TC=235 K. However, calorimetric measurements suggested a higher transition temperature, TA=282 K.
Recently our group demonstrated that tetragonal nanodomains exist also at T>TC.
The proposed experiment aims to map the local and mesoscopic structure of EuTiO3 from below TC to above TA by means PDF analysis at the D4 instrument.
Neutron diffraction should supply a more accurate description of Eu local/average structure in respect to X-rays since Ti and O positions are more accurately determined.
The accurate description of the temperature evolution of the local structure will allow to deepen the comprehension of the phase transition mechanism for this interesting magnetoelectric material..
Due to the huge absorption coefficient of Eu, this experiment is only possible at D4 instruments using lambda=0.7-0.8 Å and a double walled cylindrical sample holder. In fact, the energy dependence of the Eu absorption cross section make it unfeasible at spallation sources.

Abstract
We have successfully investigated the crystal structure of magnetoelectric EuTiO3 in the $2 < T < 300$ K interval in the real space by means of Pair Distribution Function (PDF) analysis at the D4 instrument of the ILL. Despite the huge absorption coefficient of natural Eu, we demonstrate that it is possible to collect high PDF quality patterns in about 12 hours each using lambda=0.7 Å on this Eu-rich compound.
At $T< 5$ K, beside nuclear PDF peaks also very intense magnetic ones appear due to the G-type antiferromagnetic ordering of Eu^{2+} ions.

Report.

Aim of the experiment was to investigate the local structure of multiferroic $EuTiO_3$ as a function of *T* by means of neutron-PDF analysis at the D4 instrument of the ILL.

On lowering temperature, $EuTiO_3$ undergoes a structural phase transition, from cubic *Pm*-3*m* to tetragonal *I*4/*mcm*, involving TiO_6 octahedra tilting. **[1]** The temperature evolution of the tilting angle indicates a second-order phase transition with T_C=235 K. At the same time, PDF analysis of XRPD data provided evidence of distorted nanodomains, which displayed non-zero local octahedral tilting well above T_C. **[1]**

Since the break of the *Pm*-3*m* symmetry involves mainly the displacement of the oxygen ions positions, we used neutron diffraction to map accurately the local atomic distortions.

Measurements were performed at *T*=300, 100, 45, 10, 4 and 2 K using λ=0.69706 Å instead of the usual λ ≈0.5 Å because of the strong absorption peak of ^{151}Eu around the latter value **[2]**. In fact, its absorption coefficient lowers at reducing the neutron wavelength, has a minimum around λ=0.7 Å and then it increases steeply at further decreasing λ hindering the use of spallation sources to investigate $EuTiO_3$. This unavoidable wavelength choice limited the measured Q interval to Q_{max}=16.6 $Å^{-1}$. About 12 hours were needed to obtain a PDF-quality diffraction pattern at D4.

As to the *Q*-space analysis in the $10 \leq T \leq 300$ K only the nuclear diffraction peaks of $EuTiO_3$ are present. When *T* is lowered below the Neél temperature (T_N=5.3 K) intense magnetic peaks appear at low 2θ values due to the G-type antiferromagnetic ordering of unpaired spins located on Eu^{+2} (S=7/2, L=0), while nuclear Bragg remain identical while passing through the magnetic transition. In Figure 1 are shown the patterns collected at 10 and 2 K.

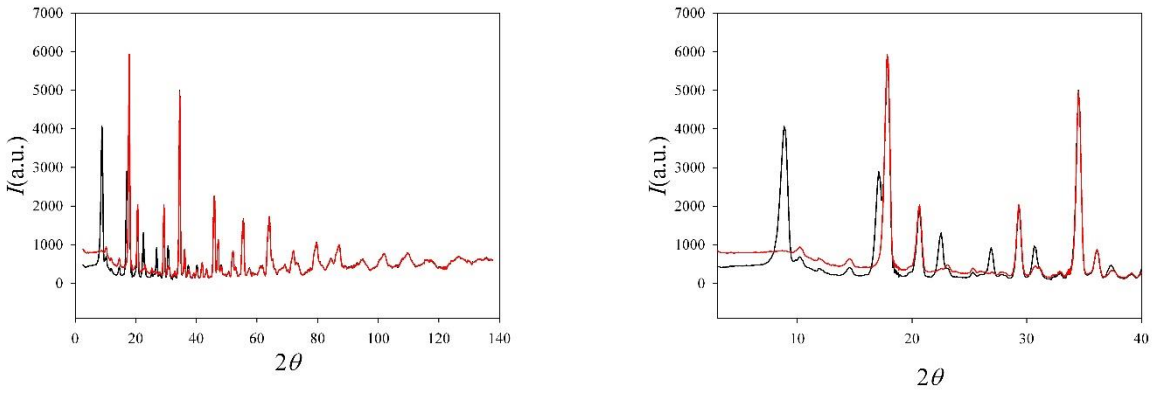

Figure 1. Black curve: NPD data at 2 K; red curve: NPD data at 10 K. Data in the full 2θ range are reported on the left hand side; the low 2θ zone is highlighted on the right hand side. Magnetic peaks are apparent only at 2K.

As to the real space analysis, in Figure 2 is shown as an example the G(*r*) of $EuTiO_3$ at 10 K. It should be noted that G(r)at 45 K (not shown) and 10 K are almost identical suggesting that atomic relaxation such as octahedral tilting already saturate at 45 K.

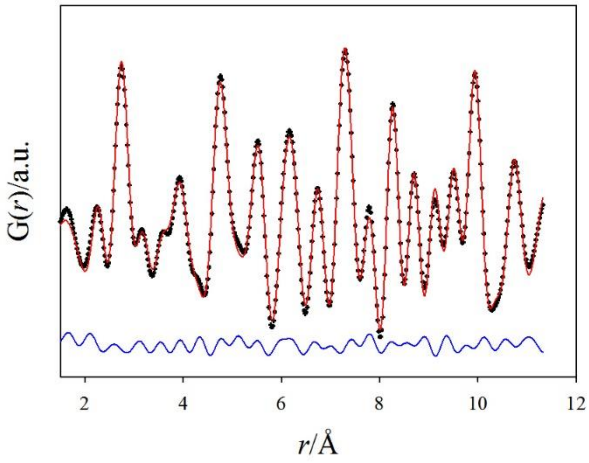

Figure 2. Fit of G(r) curve of EuTiO3 at 10 K at short *r* range. The experimental G(*r*) (black symbols) is shown together with the best fit using the *I*4/*mcm* structural model (red curve) and the residuals (blue curve)

When $T<T_N$, the G(r) function somewhat changes, in particular in correspondence of Eu-Eu distances while the remaining G(r) peaks seems to be almost unaffected.

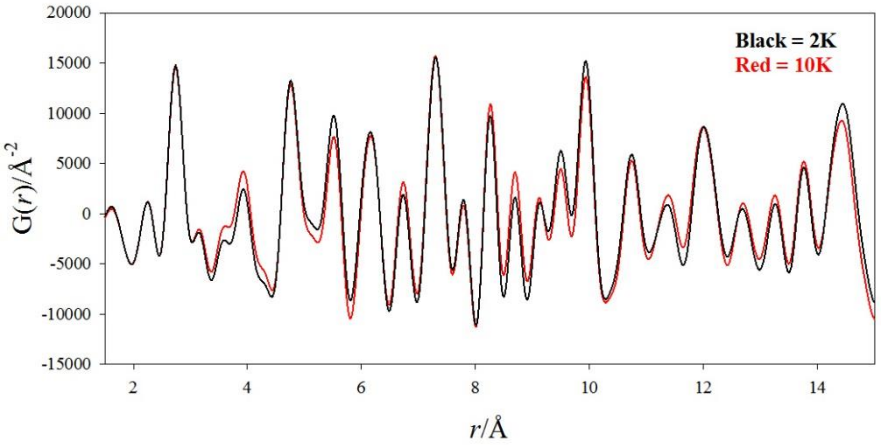

Figure 3. Red curve: G(*r*) at 10 K; black curve: G(*r*) at 2 K;

For this reason, we have supposed, as a first approximation, that the structural part does not change between 10 and 2 K, in accordance also with the reciprocal space findings shown in Figure 1. Then, we subtracted the G(*r*) curve at 10 K to the one at 2 K in order to highlight the magnetic contributions to the latter one. The dG(r) [$=G(r)_{2K} - G(r)_{10K}$] is shown in Figure 4.

The arrows in Fig. 4 are in correspondence to the Eu-distances. It is possible to note a negative peak at about 4 Å, followed by a positive peak at ≈5.5 Å, a negative one at ≈7 Å *et cetera*. Negative peaks are in correspondence to Eu-Eu distance with AF ↑ ↓ spin configurations while positive ones exist

for ↑ ↑ spin couples. dG(*r*) peaks are quite broad because unpaired spins are located on valence electrons which contribute to scattering only at low *Q* values. Moreover, beside broad peaks centred at the Eu-Eu distances, some other ones are apparent in the dG(r) curves of Figur 5, labelled with asterisks.

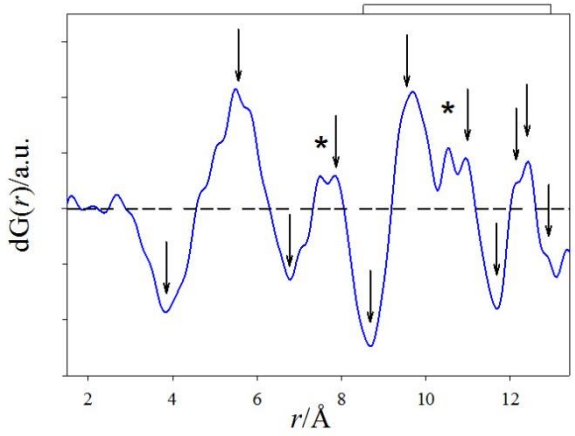

Figure 4. Blue curve: $dG(r)=G(r)_{2K} - G(r)_{10K}$; Black arrows are in correspondence of Eu-Eu distances according to the structural model at 10 K, while asterisks denotes non indexed peaks.

Work in progress:

We are at present analysing the data collected above T_N also combining the neutron diffraction data with previous XR-PDF collected at the ESRF, to map accurately the local and mesoscopic crystallographic structure of $EuTiO_3$. Moreover, we are also analysing the dG(r) curve in the framework of G-type antiferromagnetically ordered Eu atoms.

Unanswered questions and possible developments

In the above analysis, we have supposed that the crystallographic structure remain unaffected between 10 and 2-4 K, thus neglecting the possible magneto-electric coupling. The presence of peaks not in correspondence to the Eu-Eu distances according to the structural model at 10 K in the dG(*r*) curve suggests either that either the structral or the magnetic scenario are somewhat inaccurate below T_N. The use of polarized neutron below T_N should allow separating the magnetic to the nuclear contribution to the G(r) function.

It has been suggested by Petrovic et al., that at T_{sf}=2.75 K there is a spin-flop from a spin ordering along the c-axis to an ordering in the ab plane.[3]. Since the relative orientation of spins should induce different shape of the G(*r*) peaks [4], measures both above and below T_{sf} should shed light on this matter.

References

[1] M. Allieta *et al.*, Phys. Rev. B. **85**, 184107 (2012).
[2] H. Kohlmann Physica B276-278 (2000) 288-289
[3] A.P. Petrovic *et al.*, Phys. Rev. B. **87**, 064103 (2013).
[4] B.A. Frandsen *et. Al.* Acta Cryst. A70 3 (2014)