EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of clarification to the ISOLDE and Neutron Time-of-Flight Committee

P-663-Microscopic insight by nuclear hyperfine methods on ferroic Perovskites

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Requested protons:24 shifts of protons on target, (split into at least 4 runs over 2 years)

Experimental Area: GLM area, ISOLDE hall and offline laboratories 508-r-008 and r-004

We would like to thank the committee for the proposal analysis and the opportunity to explain any ambiguous aspects of our proposal. We fully understand the committee's concerns, and, with this letter, we hope to give to the INTC a straight to the point answer that definitively clarifies all the issues raised by the committee.

Firstly, we would like to emphasize the add-value of such local probe studies in these ferroic/multiferroic materials. Usually, there is a lack of experimental evidence on the theoretically claimed ferroic phases, secondly, there are several systems that have been overlooked that can be ferroelectric and thirdly, there are systems that have been attributed with the wrong ferroelectric mechanism [1-4]. We must also stress that macroscopic average crystallographic/magnetic approaches can be blind to local lattice distortions at the origin of ferroic properties. Nevertheless, this shortcoming is an opportunity for hyperfine measurements that can precisely monitor symmetry-related fine details, as we recently reported [5, 6]. In the case of *across-temperature* hyperfine studies, Perturbed Angular Correlations (PAC) is the one of the most efficient hyperfine methods since it has the same *accuracy* from 10K to 1200 K.

Additionally, we have a set of complementary techniques at our disposal, at our home institutions (e.g. X-ray diffraction, TEM, SEM, EDX, magnetization, dielectric and pyroelectric measurement), and the necessary collaboration from highly-motivated young PhD students and Post-docs (three dedicated PhD students and three Post-docs) ensuring a true effectiveness of the three teams and a timely conclusive interpretation of the research done at ISOLDE (including EFG density functional theory calculations). With such complementary means, including the singularity of the PAC technique, we have a real opportunity to decisively contribute to a detailed and comprehensive study of ferroic and multiferroic systems.

Answering the committee's first concern, two types of multiferroics were intentionally selected since they represent the two existing types of multiferroics: type I) ferroelectricity induced via a structural distortion, here the ferroelectricity and magnetization are decoupled and occur at different temperatures; type II) ferroelectricity induced via magnetic order, here magnetization breaks inversion symmetry and causes ferroelectricity, the ordering temperature is the same for the two phenomena.

With this 2-branch study we aim, on one hand, to study the particularities of each system and its order parameter temperature evolution. On the other hand, we have, simultaneously, the opportunity to offer a unified view of the common grounds for apparently different mechanisms for ferroelectricity. Thus, the challenge of understanding the different ways how to simultaneously break space-inversion and time reversal symmetries is the reason for our 2-branch study research. From our previous studies in these two types of multiferroics we believe to have the specific knowledge to tackle properly these materials. Furthermore, we have different teams focused on each system, so we do not risk having a dispersive study. On the contrary, this complementarity, with each team focused on each type of system but working together for a common aim, is our strength.

The second committee comment concerns “the implantation-induced damage”. Here it is crucial to stress that *quality* of our PAC signal (R(t) function) does not depend on the measurement temperature, as mentioned above. To further clarify this point, we should emphasize that after each implantation, and before the PAC measurements start, there is a suitable annealing procedure to recover from implantation-induced damage, and in this type of systems an annealing at 1073 K (800 ºC) for 20 minutes is usually sufficient. Nevertheless, for each new system, a implantation-induced recovery damage tests is always performed starting with annealing at lower (~300 ºC), and increasing temperatures, till we see no improvements in the PAC spectra measured at e.g. room temperature.

Thus, it is very important to clarify that although some transitions occur at temperatures below room temperature, as the switch from negative to positive thermal expansion in $Ca_2Mn_{1-y}Ti_yO_4$ (case-study ii) this does not require an extra effort compared to high temperature measurements since, as mentioned, implantation damages are fully recovered by proper annealing prior to the measurement.

Please see figure 1 where the room temperature 62K after ^{111m}Cd beam implantation and recovery annealing was performed on polycrystalline $Ca_2Mn_{0,35}Ti_{0,65}O_4$ sample. Please note the similar quality of both spectra, the difference being attributed only the physics behind the system (a structural phase transition).

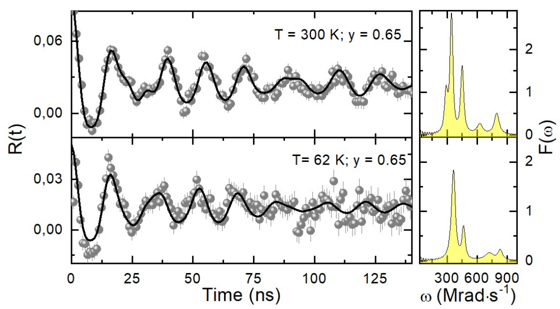

Fig.1- R(t) measured at room temperature and 62K after ^{111m}Cd beam implantation and recovery annealing on $Ca_2Mn_{0,35}Ti_{0,65}O_4$.

Thus, considering the abovementioned arguments and following the committee recommendations we will prioritize our experiments as follows:

i) Control the hybrid improper and proper ferroelectricity in the naturally-layered perovskites: focused on $Li_2ANb_2O_7$ (A=Sr), $RbA_2Nb_3O_{10}$ (A=Ca, Cd) and the multiferroic $MnSrNd_2O_7$.

ii) Probe the switch from negative to positive thermal expansion perovskites-related systems: $Ca_2Mn_{1-y}Ti_yO_4$ focused on y = 0.65, 0.53 and 0.33.

iii) Controlling improper ferroelectricity on doped rare-earth perovskites: focused on the RMn_2O_5 (R=Ho and Tb) case.

Here we should stress that the proposed systems passed already feasibility tests during the PAC proof-of-concept experiments. All of them presented very clear and wieldy spectra, warrantying a faultless analysis and exciting results. The first experimental data are very promising, already with significant information that can be seen in the proposal figures 2, 3 and 4. Thus, at this point, we have already a fully developed methodology, that allied with previous relevant experience in the field warrants the feasibility of our approach.

Having said that, we would like to mention that the minimum number of shifts necessary to accomplish our goals (considering that we are working with other users asking for the same beam) is 8 shifts per case-study. Other users have already approved beam time for the next two years using the same targets we need to extract our isotopes. Thus, with proper coordination among users, we will manage to obtain the main proposal outputs only with the ^{111m}Cd shifts. The ^{204}Pb, ^{204m}Bi and ^{111}In beams were intended as test cases and are not on our priority list.

Summarizing:

As recommended by the committee, we will first focus our study on complementary systems. They were chosen as they represent the two types of ferroelectricity/multiferroics. Different teams will focus on each case-study and in this way, via collaborative work, we expect to contribute to the search of an integrated view on the control of ferroelectricity and magnetoelectric coupling

Since, at this point, we can continue without the ^{204m}Bi, ^{204}Pb tests and ^{111}In tests, we will be able to perform our focused research with 24 shifts, although we lose the perspective for new physics exploratory ways by skipping it.

References:

[1] G. N. P. Oliveira, R. C. Teixeira, R. P. Moreira, J. G. Correia, J. P. Araújo, and A. M. L. Lopes, "Local inhomogeneous state in multiferroic SmCrO3," Sci. Rep., vol. 10, no. 1, pp. 1– 12, 2020.

[2] G. N. P. Oliveira et al., "Dynamic off-centering of Cr3+ ions and short-range magneto-electric clusters in CdCr2S4," Phys. Rev. B - Condens. Matter Mater. Phys., vol. 86, no. 22, p. 224418, 2012.

[3] A. M. L. Lopes et al., "Local distortions in multiferroic AgCrO2 triangular spin lattice," Phys. Rev. B - Condens. Matter Mater. Phys., vol. 84, no. 1, p. 014434, 2011.

[4] A. M. L. Lopes, J. P. Araújo, V. S. Amaral, J. G. Correia, Y. Tomioka, and Y. Tokura, "New phase transition in the Pr1-xCaxMnO3 system: Evidence for electrical polarization in charge ordered manganites," Phys. Rev. Lett., vol. 100, no. 15, p. 155702, 2008.

[5] P. Rocha-Rodrigues et al., "Ca3Mn2O7 structural path unraveled by atomic-scale properties: A combined experimental and ab initio study," Phys. Rev. B, vol. 101, no. 6, p. 64103, 2020.

[6] P. Rocha-Rodrigues et al., "Ca2MnO4 Structural Path: Following the Negative Thermal Expansion at the Local Scale", Physical Review B 102 (10):104115, 2020.