Assessment of the PhD dissertation

Static and dynamic magnetoelectric coupling in multiferroics

written by MSc. André Maia

I have known the student André Maia since February 2019. At that time, he came as an MSc student from Porto for a semester stay in Prague as part of the Erasmus programme. He proved to be a conscientious and hard-working student with an interest in multiferoics, and we agreed to continue working together as part of his PhD studies at the MFF UK from October 2019.

He studied a lot in the first year and so passed the state exam at the end of his first year of study. At the same time, he started his experimental work. He mastered the technique of measuring infrared reflection spectra, time-resolved THz transmission spectroscopy and Raman spectroscopy, which we use in our department to study lattice and spin dynamics from He temperatures up to 900 K. He quickly learned to fit the spectra to evaluate the parameters of phonons, magnons and electromagnons (the latter excitations are activated in the THz spectrum due to dynamic magnetoelectric coupling). At the same time, he learned to measure low-frequency dielectric permittivity (from 1 Hz to 1 MHz) and pyroelectric current as a function of temperature and magnetic field. This allowed him to study static magnetoelectric coupling.

André initially focused on studying the effect of small Fe impurity on static and dynamic magnetoelectric coupling in the classical multiferroic $TbMnO_3$ single crystals, where the ferroelectric polarization is induced by the magnetic ordering and therefore the magnetoelectric coupling is very strong. He confirmed the previously known fact that the origin of the static and dynamic magnetoelectric coupling is different in this material (Dzyaloshinskii-Moriya interaction in the first case and exchange striction in the second case), but in addition, he found that the magnetoelectric coupling in the substituted samples in low magnetic fields is strongly enhanced with a small Fe concentration (< 4%) because of the destabilization of the cycloidal incommensurately modulated magnetic structure.

Half of the dissertation is devoted to the study of ferroelectric and magnetic phase transitions in new and thus poorly studied manganate multiferroics with a quadruple perovskite structure. He discovered a THz phonon softening to temperatures of two ferroelectric transitions above room temperature in $BiMn_7O_{12}$. Thus, he proved that both phase transitions are displacive type.

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In addition, he discovered weak dielectric anomalies at two magnetic phase transitions below 60 K induced by magnetoelectric coupling.

In $BiMn_3Cr_4O_{12}$ he discovered a completely new phenomenon. He found that the ferroelectric phase transition at 125 K, which is induced by a ferroelectric soft mode, induces the formation of an antiferromagnetic arrangement of Cr spins. In other type II multiferroics, the magnetic ordering induces a weak ferroelectric polarization. In this case, a structural change at the ferroelectric transition first time triggers the formation of a magnetic ordering.

The results of the work of A. Maia are very much appreciated. The dissertation includes four publications in very good journals (PRB, PRM, J. Eur. Ceram. Soc.) where the student is the first author. In addition, he has also contributed to two articles that are not part of the dissertation. This shows the quality of the applicant's results.

The student has demonstrated the ability of independent creative scientific work and therefore I recommend awarding him the degree of Ph.D.

Prague, September 12, 2024

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