Evaluation report
Magnetoelectric multiferroics: From static via dynamic magnetoelectric effect to nonlinear light-matter interaction
Ph.D. thesis
by Jakub Vít

The topic of the thesis is highly up-to-date: multiferroic materials and magnetoelectric effects, including directional dichroism where one of the advisors of the candidate and other members of the research group he works in, did pioneering work. These substances have been of exceptional interest in the last years, both because of their importance for fundamental physics and for applications in magnetic devices. The work has been performed in broad international collaboration, with the best laboratories in Europe working on this topic and equipped with state-of-the-art instrumentation, complemented with measurements in specialized accelerator-based user facilities. Thus both the choice of topic and work environment is an excellent one.

The 169-page long thesis consists of seven chapters. The first two are introductory and present the theoretical background and the experimental methods, respectively. Results are presented in the next four chapters, 3 through 6, grouped together by specific materials that exhibit different magnetoelectric effects: directional dichroism induced by electric field and tilting of the magnetic-field in $Ba_2CoGe_2O_7$ (Chapter 3), detection of electromagnon excitations in hexaferrites by THz and Raman spectroscopy and derivation of selection rules based on the exchange striction mechanism (Chapter 4), search for nonlinear THz absorption by electromagnons in multiferroic hexaferrites (Chapter 5), and selection of magnetoelectric domains by static and oscillating electromagnetic fields in $LiCoPO_4$ (Chapter 6). Chapter 7 contains supplementary material to chapter 5.

The dissertation reports high-quality experimental results with ingeniously planned measurements and explanations that need novel theoretical insights. These were in part provided by coworkers, and their role is specified throughout the thesis. It is obvious that the candidate understands the theoretical framework of interpreting the results very well. This synergy between theory and experiment is a significant strength of the thesis.

This project, on a still unexplored ground, had to overcome special challenges. The materials are complex, with subtle changes in composition or structure leading to significant effects in the electric and magnetic properties. This variety has to be taken into account even when repeating certain measurements or when comparing single crystal data with those of ceramics and powders. To extract the principal interactions from the data and decide which ones to consider and which to neglect, requires significant experience that could only be collected through hard work both in time and in scope. This work has been obviously put into the experiments and the interpretation of data, even including re-evaluation of earlier results by the candidate. The details of the experiments are given to the extent that it is easy to follow what was measured and why. The obvious difficulties of such a complex experimental work are treated in a very clear and honest way, it is always explained if further results could not be obtained because of technical problems.

This intention to include everything, however, makes the thesis too long and somewhat uneven. It seems that the intention to document every experiment won over the requirement to put them in a consistent frame and extend the introduction beyond the one included in typical journal publications. It would have been preferable to concentrate on finished and consistent work, and giving less space to speculations about experiments that did not show the expected outcome or where the results cannot be explained at the moment. This would have made the thesis much more readable. This is also

reflected in the thesis points that combine actual results with the description of experiments that does not belong here.

All findings presented are novel and interesting, and clearly merit more detailed further investigation; in a thesis, though, a clear line has to be cut between what has been in fact achieved and what has to be done in the future. In this respect, I find that both Chapter 5 and the second part of Chapter 6 could have been significantly shortened. Chapter 5 seems a little speculative, searching for possible nonlinearity, and not simply asking the question "what happens at high intensities?". In other words, the model is first and the search is for signs in the experiment that support the model. In Chapter 6, the ultimate experiment foreseen, using intense THz fields for poling, did not give the expected result. The reasons were suspected to lie in the experimental setup, most probably thermal effects connected to the sample holder, and rather preliminary explanations are put forward. As the thesis contains enough clear and well-resolved results, these could have been left for later.

What is missing and should have been added more emphasis instead, are the contributions to the experimental arrangements only sporadically mentioned in various chapters; the experimental innovations should have been summarized in Chapter 2.

As to the broader context, the principal mechanism that connects all phenomena is domain dynamics and the change of domain population induced by poling effects. However, no detailed introduction on this very important and fundamental process is given in Chapter 1, except references to publications. During the defense, please explain the poling in detail.

Six publications resulted from the thesis work, mostly in very high profile journals (two Physical Review Letters, two Physical Review B, one Journal of the Physical Society of Japan, and one is Ferroelectrics). This output significantly exceeds the publication requirements of the Doctoral School.

Comments and questions:

- The term "magnetoelectric annealing" is incorrectly used throughout the thesis. Annealing is a process where a sample is heated, kept at some higher temperature and then let it cool slowly. The term is applied correctly when describing preparation details (page 31: "... the samples for static measurements were annealed in an oxygen atmosphere at 900 °C for 7 days", page 65: "hexaferrites are usually annealed in oxygen atmosphere"). In case of magnetoelectric materials with the Néel temperature above room temperature, e.g. Cr_2O_3, the use of "annealing" is justified, but with these low-T_N materials, where the thermal treatment means simply the cooling of the sample, it is not (e.g. page 56: "ME annealing from high temperatures"). In the publications, this expression is not present, "cooling below T_N" is written instead. This would have been more fortunate to use throughout the dissertation and in Thesis point 4 as well.

- While I highly appreciate the comparison with the theoretical background being evaluated, I would not call the discussion of electromagnon strength in Section 4.3.5 "quantitative". It is at most semi-quantitative, explaining trends in the intensities of certain modes with magnetic field.

- In some of the figures, the use of colors is not optimal, the curves cannot be easily assigned to the legend (Fig. 1.4, Fig. 3.5), the "small black arrow" in Fig. 6.9 is really tiny, inconsistensies occur between the figure captions and the text (Fig. 4.3).

- The References section, unfortunately, was not compiled with enough care. Many items lack bibliographic details: items 39, 43, 90, 140, 147, 221, 233 and 252 are incomplete (this can seem small compared to the 252 items overall, but they include even papers by the closest collaborators), the others are also often inconsistent (upper-lowercase, journal names used either abbreviated or full, issue number given or not, date as month or year only). I suggest to add a corrected bibliography that will be deposited together with the thesis, in standardized form (minimum content: standard abbreviation of journal name, volume, page or article number, year). Automatic export from journal databases is not sufficient in this case.

- p. 35. Raman spectroscopy: what is meant by "the effect is off-resonant"? Is it possible to apply Raman spectroscopy under resonant conditions in this type of measurements?

In summary, this thesis presents the results of an extraordinary project in a scholarly manner, although the organization leaves space for improvement. I accept all the thesis points as new scientific results (with the remark that the presentation could have been more concise and to the point), and recommend awarding the PhD title.

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