Referee report on the PhD thesis

“Spin and Lattice Excitations in Multiferroics”

by **Ms. Styliani Skiadopoulou**

Multiferroics, materials with coexisting ferroelectric and magnetic orders, received much attention recently owing to the strong coupling between polarization and spin degrees of freedom in these compounds. Beside the fundamental interest in materials with cross-coupled order parameters and their excitations, multiferroics are promising for applications as sensors, energy efficient memory and logic devices, where the electric field control of their magnetism can be exploited. Ms. Styliani Skiadopoulou contributed to this active subfield of contemporary condensed matter physics by studying the low energy spin and lattice excitations of several multiferroic compounds.

The thesis follows the usual structure of a PhD dissertation. After the introduction of the scientific background and the measurement techniques in chapter 1 and 2, respectively, the main results are discussed in chapter 3. This chapter is logically divided into sections according to the studied multiferroic materials. However, the introduction in the beginning of each section often unnecessarily repeats the ideas and sentences of the first two chapters. Especially in section 3.1, I missed the precise introduction of the complex magnetic order of $BiFeO_3$ in the text or rather in a figure since its non-trivial structure may not be evident for a general reader. Finally, the main achievements are summarized in the last chapter. The thesis is illustrated by several nicely edited informative figures, and the long list of references reflects the PhD candidate’s deep knowledge of the corresponding literature.

Ms. Styliani Skiadopoulou used several different experimental techniques such as neutron and X-ray diffraction, magnetization measurements, IR, Raman and TD-THz spectroscopy to characterize and study multiferroics. From the thesis it is not clear, but probably she even took part of the synthesis of the ceramic samples and ab-initio calculation of the crystal structure of Pb_2MnTeO_6. (If necessary, the PhD defense committee might clarify in which part of the experimental work the candidate was involved.) Beside her outstanding activity in the experimental research she thoroughly discussed the results of the measurements in comparison with group theoretical and ab-initio calculations as well as in the light of former results published in the literature.

In case of the room temperature multiferroic $BiFeO_3$ she extensively studied the infrared active phonon modes in ceramics and thin films samples. The candidate observed some spin-wave modes for the first time using IR spectroscopy. In the newly synthesized Pb_2MnTeO_6 the sequence of structural and magnetic phase transitions were studied by numerous methods, and it was identified as a rare example of an antipolar antiferromagnet. Finally, the spin and lattice dynamics were studied in Ni_3TeO_6 and related compounds. The results can shed new light on the large magnetoelectric susceptibility detected in these compounds.

Below, a few errors are listed and then some questions are asked what are raised while I was reading the thesis.

Minor errors:

- On the cover “Prague 2016” is written but according to other documents it should be “2017”.
- In the end of section 1.1.2.1 it is stated that the AFM phase of $YMnO_3$ does NOT break time-reversal symmetry, however, the spin is always reversed by the time-reversal operation. (The cited paper does not mention time-reversal symmetry in this compound.)
- In page 21 the DM interaction is introduced for a 180^o bond. In the discussion it is not clearly mentioned that the bond should be distorted to break the inversion symmetry as otherwise DM interaction is not allowed as shown by T. Moriya (Phys. Rev. 120, 91 (1960)).
- In page 23 “the divergence of the exchange interaction J” is discussed. Divergence is defined for vector or tensor fields. Without the definition of J, whether it is a scalar as usually or a tensor, the above statement is not clear.
- Figure 1.11 is not consistent with equation 1.44. The Brillouin zone should be halved for the antiferromagnetic chain.
- When both ε and μ differ from 1, equation 2.8 is not correct as it should contain the surface impedance instead of the refractive index.
- In figure 3.3 and 3.5 the citations are wrong.
- In page 68 the square root symbol is missing from the expression of the refractive index
- In page 82 the factor group analysis shows that Pb_2MnTeO_6 should have 15 IR active phonon modes in the case of space group I2/m. However, 16 phonon modes are detected experimentally. In page 83 and 84 several possible scenarios are listed to explain the extra mode. Thus, the following claim of the conclusion (page 87) is unjustified: “The number of phonons observed in the IR and Raman spectra correspond to the number of phonons expected from the factor group analysis in both phases.”
- In page 101 the space group of Ni_3TeO_6 should be R3, and instead of Iα-3 the notation Ia-3 should be used.
- In figure 3.23 the unit of magnetization should be the same on both scales for better comparison.

Questions related to the thesis:

- What can be the microscopic origin of the irreversible change observed in spin-wave spectrum of $BiFeO_3$ after the application of an external magnetic field?
- In page 64 there is a note that “the remarkable softening of the modes below 150 cm^{-1} upon heating” is observed in $BiFeO_3$. When the phonon frequencies are plotted as a function of temperature can you discard phonon-phonon scattering due to lattice anharmonicity? (Such plot could also help the reader of the thesis.)
- How does the absolute value of the dielectric constant determined from measurements on ceramics compare to the powder average of the single crystal data?
- According to the thesis (e.g. page 71 and page 91), the simultaneous presence of an excitation in both the Raman and the IR spectra measured on a ceramic sample guarantees

that the excitation is electric dipole active. How can conventional one-magnon scattering and its magnetic dipole excitation be excluded?

- Magnetic and dielectric properties of the new multiferroic compound Pb_2MnTeO_6 are extensively studied. Since this work was motivated by the magnetoelectric properties of multiferroics I am wondering if the magnetic field dependence of the dielectric function or the electric polarization has been measured by the candidate or reported by others?
- The Co analogue of Ni_3TeO_6 is assigned to be an easy-plane antiferromagnet. On the other hand spin-flop transition is observed in these materials, which is not allowed in easy-plane systems. How can you resolve the apparent discrepancy?

Irrespective of the answers to my questions, I found that the new scientific results published in the thesis certainly attract the attention of the community and prove Ms. Styliani Skiadopoulou's ability for creative work. In conclusion, I recommend awarding PhD degree to Ms. Styliani Skiadopoulou.

Budapest, August 23rd, 2017.

Dr. Sándor Bordács