

Review Report on PhD Thesis

Faculty: **Central European Institute of Technology
Brno University of Technology in Brno**

Academic year: **2023/2024**

Student: **Ing. Jana Dubnická Midlíková**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **doc. Dr. Ing. Petr Neugebauer, Ph.D.**

Reviewer: **Dr. Premysl Marsik**

PhD thesis title: Development of Fourier Transform InfraRed Spectroscopy in High Magnetic Fields

Topicality of doctoral thesis:

The presented thesis of Ing. Jana Dubnická Midlíková deals with construction of high magnetic field FTIR spectrometer and can be positioned between the fields of experimental physics and physical engineering.

It has proper structure with introduction and clearly defined aims, sufficient body of the text, conclusion, comprehensive bibliography, and includes also curriculum vitae of the author, which documents her academic activities, contributions to conferences and workshops, and several scientific visits to institutions in Europe and overseas.

Meeting the goals set:

The defined goals – construction of high-field FTIR spectrometer, and performing the initial measurements on single molecular magnets and 2D materials – are fulfilled completely.

Problem solving and dissertation results:

It is clear that lot of work has been done by the thesis' author on technical parts of the instrument and its commissioning. Obtained results were published in relevant journals.

Importance for practice or development of the discipline:

The constructed instrument will be further utilized for studies of novel materials and is a part of broader project. It is rather unique setup which allows measurements at fields up to 16 T in a laboratory, without the need of complex and expensive liquid Helium infrastructure.

Formal adjustment of the thesis and language level:

Thesis is well structured, formatted and contains sufficient and clear figures. Small discrepancies will be addressed below. English language is appropriate for the scientific content.

Detailed review:

The main text is structured to four chapters: 1. Theoretical background, 2. FTIR Magneto-Spectroscopy, 3. Experimental Setup, 4. Magneto-Optical Measurements. Each chapter sets slightly different style and level of detail. In the following I will comment on the chapters one by one, in the order of the document.

First chapter is named Theoretical background, although – apart from the background of electromagnetic radiation and its interaction with matter – it contains also some practical aspects of the experimental methods. The structure of the chapter feels bit disordered. It would be better if the mathematical parts: Maxwell's equations, Lorentz model, would appear together, while the more general text about light spectrum and infrared radiation could be positioned after. I found the history of infrared spectroscopy very interesting and pleasant to read.

However, the section 1.3 Infrared spectroscopy has very clumsy start with one sentence repeated twice, stating that "IR spectroscopy is based on the vibrations of the atoms of a molecule... providing detailed information about molecular vibrations", and part of the same sentence appears again in beginning of subsection 1.3.2.

Section 1.3.3. on page 20 introduces the Lorentz model of the dielectric function and only briefly mentions that this model also covers free electron response when resonance frequency is set to zero. It would be helpful if the complete Drude-Lorentz formula appeared in the text. On the following page the resonance line-shape is plotted in terms of dielectric function and complex refractive index, although the relationship between N and ϵ is never expressed. Similarly, the text does not give relation between the extinction coefficient k and absorption coefficient α . Eventually, that part would also benefit if the relation of dielectric function ϵ and optical conductivity σ was mentioned.

Chapter 2 named FTIR Magneto-Spectroscopy introduces, rather briefly, selected magneto-optical phenomena: Electron Paramagnetic Resonance, Zero Field Splitting, and Landau level transitions, together with overview of single molecular magnets and 2D materials – these are the effects and materials that would be further studied with the finished magneto-spectrometer and so naturally preface the results reported later in the chapter 4.

There is some typographical disorder in the presentation of the spin Hamiltonian on page 49, mixing bold/plain symbols with hats/no hats. It is difficult to follow which symbols represent vectors or tensors and some of the symbols are not properly introduced.

This theoretical text very quickly turns into practical details of EPR vs FTIR spectroscopies, which would be better positioned near the last part of the chapter, which presents overview of existing laboratories equipped with infrared instruments and high field magnets.

Chapter 3 details the instrument that has been built by the thesis' author. The main parts are Bruker 80v FTIR spectrometer and closed cycle cooled superconducting 16 T magnet with variable temperature insert. Jana Dubnická Midlíková designed and constructed probes that are inserted into the magnet and couple the IR radiation from the spectrometer through the sample to the detector. There are 2 probes, labelled as A and B, one (A) leads the radiation to the sample and back out of the magnet towards external detector and the second (B) has the detector element placed directly under the sample (in magnet and low temperature environment). It is bit unfortunate that the purpose, advantages or disadvantages of the two designs are not discussed immediately when the designs are introduced, only couple of pages later.

I see certain weakness of the design in the fact that only single off-axis parabolic mirror is used for aligning the beam to the sample and detector. The mirror, reflecting and focusing the parallel beam from the FTIR auxiliary output port down towards the probe, is mounted on a tilt stage that has two degrees of freedom and one of them, horizontal tilt, is likely not very useful. From the thesis, it is not evident if the beam path geometry was checked and optimized. Especially for the probe A that brings the light to external detector, large amounts of the radiation might be lost on internal reflections – as is mentioned in the text.

I appreciate that also technical aspects of the work are discussed, as 3D printing, soldering electroplating and polishing – the internal surfaces of the light tubes have been polished using rifle barrel polishing kit. I find that ingenious.

Eventually, various tests of the setup have been done, and the most critical – IR signal test – is presented at the end of the chapter 3. It is great that decent signal can be obtained in various configurations of elements spanning the whole IR range (FIR/MIR/NIR), which is presented in practical table 3.3, although one might ask how representative are the “100% line” spectra, when some show large systematic deviation, up to several percent. Comparison of the signals obtained through the probes with some reference spectra recorded directly with the Bruker internal detector would also be useful, to get some general idea about the amount of light that is lost in the extended probes.

Chapter 4, titled Magneto-Optical Measurements, presents experimental data obtained with the finished instrument and also data that have been obtained on comparable setup in High Magnetic Field Laboratory in Grenoble, by the author during her research stay abroad.

The first part (4.1) of the chapter shows examples of spectra and their processing. It is written in single paragraph which makes it difficult to read and understand. Several symbols are introduced for different representations of the spectroscopic data: $T(B)$, $S(B)$, $R(B)$, but it is hard to grasp their relationship and purpose, especially when these symbols are not shown on the figures that

accompany the text. Still in the single paragraph, the discussion turns from the numerical manipulation to interpretation of the EPR features.

What I missed is some general explanation of the absorption features that are seen in the raw spectra already: are they molecular vibrations? Artefacts? Something else? Are they known? Although it is clear that main focus of the work is on the EPR behaviour, it would be nice to have some overview about the dominant spectroscopic features, particularly when some of them show very strong dependence of their amplitude on the magnetic field (e.g. peak near 220 cm^{-1} which seems to be present in all spectra).

Part 4.2.1 presents magneto-spectroscopic data on four Cobalt based Single Ion Magnets. Spectroscopic data are presented in several forms, before and after normalization steps introduced before. I would prefer if the figures related to one compound appear together, and not scattered over several pages. Eventually, the serial normalization of subsequent field-dependent measurements reveals several features changing frequency as a linear function of field. The text states that their origin is not exactly known, but to me it seems that for each compound one of them have just been identified and attributed to EPR with ZFS.

Finally, the same Cobalt SIMs were measured on the newly developed high field spectrometer in CEITEC. Evidently, the setup can produce high quality far-infrared spectra, comparable with established laboratory in Grenoble HMFL. Near-infrared performance is also demonstrated with Landau level spectroscopy of germanium.

In summary, the presented thesis fulfils criteria for doctoral dissertation and documents that the student Ing. Jana Dubnická Midlíková performed significant work on designing, developing and commissioning the spectroscopic instrument.

Typography errors and small omissions:

Page 11 eq. 1.10: μ_0 in place of ϵ_0

Page 21 eq. 1.23: irrelevant $\gamma\omega$ in numerator

Page 26 just above eq. 1.29 “ .. function of deceleration, $S(\delta)$ ” should be *position*, not *deceleration*. Further, in eq. 1.29, the whole argument of the cosine should be in parentheses.

Page 28 eq. 1.35 should have factor 2.

Page 31, paragraph about Jacquinet’s advantage: “monochromators with entrance and exit..” seems the word *slit* is missing.

Page 34, part about semiconductor detector, sentence: “The photon energy in semiconductor detectors is greater than the bandgap..” somehow missing a conditional if/when; semiconductor detector will not be sensitive to photons with lower energy.

Page 51 text below equation 2.5 refers to eq. 2.6, should be 2.5.

Page 57: name of Dr. Milan Orlita is misspelled.

Page 58, typo: $T=5\text{-}300\text{ K}$ (not cm^{-1})

Page 84 figure 3.14 seems to have caption from figure 3.12.

Questions and comments:

- Spectroscopies are not necessarily only electromagnetic: what are examples of spectroscopies that do not deal with spectra of electromagnetic waves?
- Drude-Lorentz model: the Drude term is not explicitly written in thesis. Strength of phonons is measured by “plasma frequency”: what does plasma frequency mean?
- Fourier transform is presented as integral in the text. How is the Fourier transform actually calculated by the computer? What is the complexity of the calculation of discrete FT compared to Cooley-Tukey FFT algorithm? What is the role of filling factor mentioned on page 112?
- Superconducting magnets: on page 41 it is written that SC magnets can carry much larger currents than ordinary wires. But superconductors have limit in the current they can carry, and also superconductivity can be destroyed by high magnetic fields. What kind of material is used for the wires in the used 16 T magnet (if it is known), what is the T_c , how close are the currents to the critical current, what would be the critical field and does it really matter?
- On page 45 where EPR is introduced, only free electron Zeeman splitting is discussed. What happens in material environment? What can we learn from EPR spectra? Similar for the ZFS: what mechanism is responsible for ZFS, what are characteristic values in materials? The text on p. 94 and further mentions that “spectra did not provide enough resolution for the determination of the precise g-tensor, only g_{iso} was determined in simulations.” Would higher resolution IR spectrum provide enough information, or the resolution is limited by some other influences?

Conclusion:

In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

In Fribourg, 30.11.2023

Dr. Premysl Marsik

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