Report on the doctoral thesis of Ms. Kristina Vlaskova

In the doctoral thesis entitled "*Magnetic properties of rare-earth $A_2Ir_2O_7$ pyrochlore iridates*", Ms. Vlaskova provides a thorough and high-quality work on the chemical synthesis and physical properties of pyrochlore iridates. The outline of the manuscript follows a usual scheme: background, methods, state of the art, results and conclusions. The manuscript is prepared according to excellent standards in terms of visual presentation of the concepts and data in figures as well as in the overall layout and referencing. The manuscript is about 100 pages long and contains a lot of text, which appears entirely original to the best of my knowledge. In part 4 – the presentation of the results, some of the phrasing and organization of ideas could have been better optimized in order to best convey the important messages, improve the clarity and ease the reader with retrieving factual information from the text. This, however, does not compromise the quality of the work nor the scientific reasoning conveyed in the text. The overall shape of the manuscript appears very appropriate for a doctoral thesis.

In part 1, the fundamental concepts relevant to a work on pyrochlore magnets are adequately introduced – single-ion magnetism including spin-orbit coupling and crystal-electric fields, magnetic frustration, and some fundamentals of solid-state synthesis. This part is kept concise while providing an appropriate level of details in view of the scope of the work reported in this doctoral thesis.

Part 2 introduces all experimental methods used in this work. Comments concerning part 1, in terms of clarity and appropriateness of the content, also apply to part 2. In both part 1 and 2 the author manages to provide an original and personal description, which is always appreciable.

Part 3 is a 3-pages long state of the art on the crystal structure of pyrochlore oxides and electronic states in pyrochlore iridates. The content and level of details are appropriate, but some more details emphasizing the global motivation for these studies would have been appreciated.

A large amount of experimental work for this doctoral thesis was devoted to the synthesis and characterization of samples, which both come with challenges and are exposed in part 4.1. The corresponding paragraphs manage to convey a summary of difficulties and attempts to circumvent these in the synthesis of pyrochlore iridates. It is an important point and a strength of the present doctoral thesis to adequately account for these steps.

Bulk thermodynamic properties of the heavy rare-earths are presented and discussed in details in part 4.2. The quality of all the experimental data concerning the physical characterization of these samples is remarkable, denoting a dedicated and careful laboratory work. This is another major strength of the doctoral thesis and continues with part 4.2 where high-quality inelastic neutron spectra of Er and Tm iridates are presented and exploited to extract rare-earth single-ion properties. This knowledge is then used to compare with the bulk thermodynamic data using mean-field calculations. The agreement, discrepancies and limitations are appropriately discussed, revealing the good scientific approach and reasoning of the candidate. Muon spin rotation experiments are presented in part 4.5, providing essential information on the magnetic ordering of iridium ions in the studied samples. There again both the quality of the experimental work and its analysis are expertly done and solidly presented. The last part of actual results, 4.6., provides a summary of AC magnetic susceptibility measurements. The quality of the data is once more remarkable. The usual phenomenological models to evaluate the possible origins of the dynamics are applied and compared, and the conclusions are adequately discussed in view of other works having evidenced the role of domain walls in pyrochlore iridates.

In summary, the manuscript qualifies as an original scientific work and provides high-quality experimental results that bring significant and new contributions to an important field of condensed matter research. The results obtained on the Tm compound particularly stand out as they potentially reveal a rather unique behavior among rare-earth pyrochlores. Another strength in terms of results comes from the comparison of the different samples, for which all physical characterizations were consistently performed and analyzed, providing clear evidence for important similarities in these materials. The long list of publications by the author of the thesis, in peer-reviewed journals, further confirms the commitment of Ms. Kristina Vlaskova and her ability to produce creative scientific work. A few important points in the manuscript deserve some readjustments that I can address separately through a list of suggested corrections.

Questions

- The words ‘entanglement’ and ‘emergence’ are repeatedly used throughout the manuscript, not always where one may expect these nowadays. Can you give explain these two words in the context of modern condensed matter physics relevant to the present work?

- What makes rare-earth pyrochlores effectively described as systems with pseudo-spins S=1/2 ?

- For rare earth ions, it is sometimes necessary to treat both crystal-electric field and spin-orbit coupling non-perturbatively in what is called the "intermediate coupling scheme". Can you introduce this and consider what would be possible consequences for the analysis of the experimental spectra of crystal-electric field excitations?

- The conclusion of the crystal-electric field analysis for the thulium-based iridate is that the ground state is a singlet, well separated from the first excited state. Can you put this result in a wider context? What are examples of similar situations in general and in pyrochlore oxides in particular? What interesting physics may this situation lead to?

- The conclusions of the crystal-electric field analysis of the thulium-based iridate are heavily based on the exclusion of a mode at 4 meV that is ascribed to Tm_2O_3 impurities. However, this mode appears quite intense while the manuscript also states that Tm_2O_3 impurities amount to a volume fraction of less than 1.5%. Can you quantitatively demonstrate that the level at 4 meV in the INS data can be excluded based on this volume fraction?

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