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Review of the doctoral dissertation of Wojciech Marcin Marciniak, M.Sc., entitled: "Influence of structure and composition on properties of Fe-based magnetic materials—a DFT study"

The doctoral dissertation of Wojciech Marcin Marciniak, entitled: "**Influence of structure and composition on properties of Fe-based magnetic materials—a DFT study**" was written at the Institute of Physics, Faculty of Materials Engineering and Technical Physics Poznań University of Technology under the supervision of dr hab. inż Mirosław Werwiński, prof. IFM PAN. The student conducted this study mainly in Poznań with a period at the Material division of Uppsala University (Sweden), one of the main centers in the world for the study of magnetism via density functional theory.
The dissertation is in the form of a collection of papers with 5 manuscripts; 4 of these manuscripts have been published in international peer-reviewed journals, while one is currently available only on the ArXiv repository. The papers included in this Ph.D. thesis have garnered 13 citations on Scopus https://www.scopus.com/authid/detail.uri?authorId=57200118579 at the present date, which is a reasonable result considering that the papers were published in the last 2 years.
Wojciech Marcin Marciniak 's dissertation takes 87 pages plus the co-authors contribution statements. The thesis is composed by an historical and scientific guide in the first chapter. The second chapter contains the 5 manuscripts, while in the third and last chapter there is a short summary of the published results.

Section 1 begins with a broad historical introduction on the relevance of rare-earth free ferromagnetic materials with large magnetocrystalline anisotropy energy (MAE). It is followed by subsequent subchapters in which there is an introduction of the computational setup, including which software and which equations have been used for the main results. The chapter continues with the description of the present and future technologies involving Fe-based compounds as HAMR devices, which are developed in companies like Seagate Technology mainly in the last 10 years. This chapter ends with a brief description of all manuscripts which are reported in Section 2

Section 2 is the core of the thesis. It consists of 5 subsections where the author reported the 5 manuscripts. Paper I is on a Fe-based antiferromagnet while papers II, III and IV are on FeCo under compression or doping. Finally, paper V is about the hard phase $L1_0$ FePt.

Subsection 2.1 reports a combined theoretical-experimental paper on the Fe-based antiferromagnet $YbFe_4Al_8$ that was published in *Journal of Alloys and Compounds*. Marciniak is the first and corresponding author.
The authors found that the magnetic ground state of this compound is in the so-called C-type antiferromagnetic phase. Once established the ground state, they performed theoretical calculations for other properties such as the Mulliken electronic population, electron occupancy and distance of the DOS peak from the Fermi level. The overlap between the theoretical and experimental results is limited, the author suggested that additional studies are necessary to fully understand some details of the Yb magnetism.

Subsection 2.2 reports the only manuscript published exclusively on the arxiv repository. The Ph.D. candidate is first and corresponding author. The paper reports the MAE and the Curie temperature in $Fe_{1-x}Co_x$ alloy as a function of doping concentration and structural deformation. They use the DLM method typically overestimates the critical temperature by approximately 30%.
Although this topic has been previously studied by several authors, Marciniak et al. claim to have explored a broader range of structural deformations, which had not been investigated in the literature. They also proposed a novel Brugers pathway involving a new crystal structure.

Subsection 2.3 is devoted to a paper published in *Physical Review B* where the Ph.D. candidate is first and submitting author. The authors extensively study the alloy $(Fe_{1-x}Co_x)_{16}C$ reporting the MAE, average magnetic moment, entropy and enthalpy as a function of doping concentration and structural deformation. To account for the various chemical combinations, the authors used the virtual crystal approximation and coherent crystal approximation in combination with the special quasirandom structure. From a methodological perspective, the authors claim to have developed a more efficient method for determining calculated properties, which could also be applied to other FeCo alloys with doping. From the scientific point of view, their main novelty of their results is a positive correlation between MAE and mixing enthalpy.

Subsection 2.4 includes a paper published in *Journal of Alloys and Compounds* where the Ph.D. candidate is the second author. The study combines experimental and theoretical results in 5d-doping of $(Fe_{0.7}Co_{0.3})B$. According to the literature, the first author, A. Musial, appears to specialize in experimental work; however, this is not explicitly clarified in the statement. If this is the case, the Ph.D. candidate would be the first among the theoreticians which indicates a strong contribution at least on the theory side of the paper. The theoretical team suggested to the experimental team what is the ideal doping and crystal structure to enhance MAE in $(Fe_{0.7}Co_{0.3})B$ creating a reasonable overlap between the experimental part and theory part. The theoretical results are limited to the first 4 figures, where the authors present MAE, spin and orbital magnetic moment of the 5d-doping and DOS.

Subsection 2.5 reports the paper published in *Journal of Magnetism and Magnetic Materials* where the Ph.D. candidate is the second author. This paper reports only theoretical results and it is the most cited paper of the collection. From the statements, It seems that the Ph.D. candidate performed the calculations in SPR-KKR and the first author J. Marciniak made the calculations in FPLO. The authors calculate the total energy as a function of the c/a ratio, the polar angle of the spin and the size of the magnetic moment. The results are numerically more solid due to the large amount of heavy element Pt, they have a MAE that is one order of magnitude larger than FeCo-based systems. Of course, the drawback for the technological applications is the large price of Pt.

The thesis concludes with **Section 3**, which provides a summary and conclusions about the presented papers, highlighting the main results of the research. This section is followed by a popular summary, references, and statements from the authors.

After analyzing the above result, I have some remarks, a general question and some questions on the listed manuscript. I will report the questions on the publications, writing the roman number of the manuscript and consecutive letters for every question

1) I request the Ph.D. candidate to provide a description of all sources of magnetocrystalline anisotropy, including shape anisotropy and dipole-dipole magnetic interaction, and to explain why these factors are not relevant in the systems studied in this Ph.D. thesis.

IA) About paper I, can the Ph.D. candidate investigate whether the system is an altermagnet? The concept of altermagnets, introduced in 2020, was summarized in two PRX papers in 2022. https://journals.aps.org/prx/abstract/10.1103/PhysRevX.12.040501 and https://journals.aps.org/prx/abstract/10.1103/PhysRevX.12.031042 and a Nature Communication https://www.nature.com/articles/s41467-023-40877-8 . The Ph.D. candidate could just perform non-relativistic band structure and observe if there is non-relativistic spin-splitting, for instance, along the k-path between the Gamma point with coordinate (0,0,0) and the R point with coordinate (0.5,0.5,0.5). There are very few altermagnetic metals, and many members of this family of materials could host this phase with a possible anomalous Hall effect.

IB) It is strange that the authors conclude that U_{4f} should be zero. Usually, U_{4f} is necessary for a good agreement between the theoretical and experimental position of the 4f peak in the DOS. The position of the 4f seems at -5 eV, why have the authors not concluded that the value of U=10 was the best to fit the experiments??

IIA) In paper II, I guess that the authors should correct the first formula replacing $T_C^{DLM} \rightarrow T_C$ as the authors wrote in equation (1) of paper V.

IIB) In Figure 1, the authors have some maximum and some minimum of the MAE of around 0.3 eV. The authors correctly used a huge number of k-points to reach extreme accuracy, however, due to the small value of the MAE, but I have the feeling that the main results will not be stable anyway with a different exchange functional, as instead is not happening in paper V. Will the results partially stay with another functional??
We can see this from another point of view. We should consider that T_C is around 1000 Kelvin, which in energy is 86 meV. An error of 30% (claimed by the authors for the DLM method in paper II) on 86 meV is equal to an error of around 27 meV. This error of 27 meV can be reduced if we consider the error per single atom, but we are still around 2 orders larger than the estimated MAE. Why are you confident about your estimated MAE of the order of 0.3 meV or less??

IVA) In paper IV, I can expect that the results for 3d and 4d would be similar in Figure 2. However, it is very strange that among the 5d elements, just W influences the MAE while the Pt and others have the same influence of 3d/4d materials. Does the Ph.D. candidate have something to comment on beyond what is already written in the paper?

In summary, the motivation for this research is presented clearly and with precision. The thesis is well-edited, and the text is legible and grammatically accurate, making it easier to analyze and evaluate the results. All the theoretical figures (most of them are likely obtained from the Ph.D. candidate) in the five papers are very detailed, striking and well-structured. The research conducted by the Ph.D. candidate is part of the current trend in the scientific community related to the long-term interest in free-rare earth materials. The publications in the paper collections have appeared in peer-reviewed international journals with a significant impact factor. The Ph.D. candidate is the lead author in the first three papers and second author in the last two papers. Taking into account the statements, he obtained the permission of the co-authors to include these results in his Ph.D. thesis.

Despite numerous remarks and questions, the doctoral dissertation of Wojciech Marcin Marciniak, M.Sc., in my opinion, meets all the quantitative and qualitative criteria for doctoral dissertations in the field of engineering and technology in the discipline materials engineering. In connection with the above, I request that Wojciech Marcin Marciniak, M.Sc., be admitted to the next stages of the doctoral procedure.