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Referee's opinion on the habilitation thesis of Dr Vojtěch Chlan

entitled:

„ Nuclear magnetic resonance and density functional theory in solid state physics"

The importance of an interplay between an experiment and theory is well known in science. The habilitation thesis of Dr Vojtěch Chlan gives a very good example of a successful application of the theory to explain experimental data. He applied the DFT theoretical approach to describe and explain the experimental spectra of the NMR and Mossbauer effect spectroscopy, caused by hyperfine interactions in solids. In particular the subject of his activity besides the NMR experiments covers the description and explanation of the spectra for the magnetic ferrites, similar compounds of complicated structure and also the nonmagnetic compounds where the interaction of electric field gradients (efg) with the quadrupole moments of nuclei cause the quadrupole splits of the nuclear resonance lines. The author got experience in NMR spectroscopy in the research group of Prof. H. Štěpánková. With the aim to understand and explain the NMR spectra he mastered and used a powerful theoretical tool – the WIEN 2k program package based on the density functional theory (DFT). It is worth adding that the NMR spectroscopy in application to magnetically ordered materials demands a different experimental approach and interpretation than the "classical" NMR, because the signals are obtained due to hyperfine fields with zero magnetic external field, and the resonance lines are much broader. However, this technique gives a unique possibility to investigate the local magnetic interactions on inter-atomic scale. Thus, the application of DFT with extension on hyperfine interactions appeared to be a very crucial for the interpretation of the experimental results. The structures of the investigated materials posses relatively low symmetry which involves the complicated anisotropic magnetic interactions leading to the NMR spectra with many resonant lines, difficult to interpret. To observe such phenomena the author performed complicated NMR measurements on single crystal samples, which additionally proves his experimental skills.

The introduction to the set of habilitation publications presents a brief, but very clear description of the habilitation thesis concept. After the short introduction to the experimental basis and NMR principles, materials of interest and the theoretical problems, the most valuable results of his papers are briefly presented and discussed pointing to the most important conclusions.

The author presents a very successful application of the DFT theory to solve the NMR spectra and explain the hyperfine interactions in 17 original papers published in the international journals of high rank. In 6 of them he is the first author, in 9 the second. It is worth commenting that 5 of those papers are published in one of the leading physical journals, the Phys. Rev. B (impact factor 3,52). The other journals, important for magnetism, solid state physics and physical chemistry are also highly rated. All the papers were published in the period from 2010 up to 2019 year. It is also important, that a few of them were elaborated in the international cooperation with the known groups investigating materials possessing complicated structures and magnetic properties, e.g. ferrites. These are groups from the USA and Poland, Germany, France, Japan, Ukraine and New Zealand. It is easy to deduce that some of the scientists from abroad appreciating his experience asked Dr Chlan to perform the NMR measurements on their samples and interpret the results. For example, in a cooperation with the group from Krakow (Poland) Dr Chlan helped in the interpretation of the Mössbauer spectra for the high quality monocrystalline magnetite sample and he made the NMR measurements on the magnetite monocrystal provided from them. It enabled the observation and interpretation of anisotropic magnetic interactions in this monocrystal at the temperatures below the Verwey transition.

The scientific publications selected by Dr Chlan as a core of his habilitation thesis are of a very high quality and scientific value. Some of the publications are accompanied by the "Supplemental Material" where the details of calculations and interpretations given in the paper are presented. There is no need to evaluate all these publications, but let me shortly express my impressions and comments.

Since the DFT theory well describes the interactions on the electronic level, its application to the hyperfine electronic interactions with the nuclei needs special supplementary and complicated calculations, and this problem has been solved successfully by the author in cooperation with the theoretician P. Novák in the first (VC1) of the habilitation papers set. This publication is very important and can be treated as the starting point for the theoretical interpretations of experimental spectra given in the papers included to the habilitation thesis.

The second paper (VC2) concerns the interpretation of experimental NMR spectra obtained for lithium ferrite monocrystals where the shifts of resonance lines were caused by the anisotropy of the hyperfine interactions on ^{57}Fe nuclei. In the interpretation made with the use of the theoretical tool elaborated in the first publication, the positions of resonance lines were quantitatively explained as caused by this anisotropy of magnetic interactions.

In the third paper (VC3) the analysis of hyperfine interactions in hexagonal ferrites of X-, W-, and M-type in the system Sr-Fe-O is presented. The NMR and Mössbauer spectra obtained for Fe nuclei were interpreted based on ab initio calculations (DFT). The NMR lines were assigned to individual crystal sites and a preferential occupation of ferrous ions in the S blocks of the X- and W-type ferrites was observed.

The papers VC4 to VC8 deal with the hexaferrites. The paper (VC4) presents Fe NMR results analyzed theoretically concerning also the magnetocrystalline anisotropy in La, Pr, and Nd substituted hexaferrites with account on the problem of charge localization. Paper VC5 also concerns the problem of hyperfine fields origin in hexaferrites with Ba and Sr. In the papers VC6 and VC7 the ^{67}Zn NMR is reported and the obtained spectra (both for poli- and monocrystals) are theoretically interpreted using DFT for the case where hyperfine magnetic and electric interactions compete. Paper VC8 concerns the problem of interpretation of ^{57}Fe NMR spectra obtained for Y-type hexaferrite by means of electronic structure calculations based on DFT.

Papers VC9, VC10 and VC11 present interesting results for the magnetite. At first the Fe NMR results are presented, then the magnetic measurements data, and in addition Fe

Mössbauer effect measurements. There is a very valuable and detailed description of local properties and hyperfine parameters (obtained with the DFT theory) in relation to the crystal structure.

In the paper VC12 an interesting NMR research of lutetium iron garnet (LuIG) is presented. Besides of Fe NMR the ^{175}Lu NQR lines were obtained and by the use of DFT calculations the observed quadrupole splits of the lines were attributed to the Lu positions in the lattice.

Very interesting work is presented in CV13, where the ilmenite FeTiO3 was investigated by Fe Mössbauer spectroscopy and NMR on ^{47}Ti and ^{49}Ti isotopes for which electric field gradient splits of resonant lines were observed. This was interpreted by use of ab initio calculations based on WIEN program set.

In the paper VC14 an interesting and difficult ^{71}Ga NMR experiment for the gallium metal under pressure is presented giving information on electric field gradients and NMR shifts. The theoretical analysis explained their relation to the electronic structure of galium.

Paper VC15 presents NMR investigations of intermetallic compounds $LaCuAl_3$ and $LaAuAl_3$ interpreted with the help of the density functional theory. Here the most valuable from the experimental point of view are the NMR measurements on three elements consisting the investigated compound (^{139}La, ^{27}Al and ^{65}Cu), which gave an optimal basis for a complete description and understanding of the interactions existing in the investigated compounds.

In the paper VC16 Dr Chlan focussed his interest on the Bi_2Se_3 topological insulator. The single crystal was investigated with ^{209}Bi NMR what allowed to observe unusual quadrupole effects, which were also precisely interpreted.

The last paper of the set (VC17), is also very interesting. In this paper the very difficult problem of the occupation of tetrahedral sites in $Lu_3(Al_{5-x}Ga_x)O_{12}$ substitutional garnet is solved based on NMR on ^{27}Al and ^{71}Ga spectra (not so easy to obtain) and DFT calculations.

As it was mentioned before, the papers collected as the habilitation thesis represent a very high scientific value due to the presentation of experimental results, mainly NMR and Mössbauer effect, accompanied by brilliant theoretical interpretations based on the DFT theoretical approach. The characteristic common feature of these publications is a high quality experiment made on very well defined polycrystalline or monocrystalline samples and the detailed and precise theoretical calculations based on DFT theory, which fit the experiments and produce very good explanations of the observed phenomena.

The above presented analysis clearly confirms that Dr Chlan is a very talented physicist, skilled and experienced in investigations with NMR technique, who mastered the theoretical tool based on DFT theory to explain and describe experimentally observed properties and spectra of complicated compounds.

All the papers consisting the habilitation set represent valuable and original research results broadening our knowledge of the complicated magnetic and magnetoelectric materials.

The detailed plagiarism check of the habilitation thesis of Dr V. Chlan points to the parts of the texts which practically must be analogous or simillar in different works because they describe the physical concepts or material and names. In addition in all papers the elements describing NMR experiments and also the parts describing DFT theory can naturally be very similar. It is clear that the introductory part and all the papers present original and new results, scientific ideas and interpretation possessing practically no traces of plagiarism, which confirms the originality of the analyzed habilitation thesis of Dr Vojtěch Chlan.

Concluding, I am deeply convinced that Dr Vojtěch Clan is a brilliant physicist who possesses high scientific values and deserves habilitation according to the appropriate requirements and regulations in the Czech Republic.

Krakow, 25 March 2021

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