Paris, January 17th 2023

Report on the habilitation thesis of Jan Mistrík entitled “Light polarization: a probe of nanomaterials”

The report (196 pages) presented by Jan Mistrík for the habilitation degree from Charles University (Praha, Czech Republic) is composed of two main parts and of height selected articles published in international journals. According to the (auto) plagiarism audit (attached Turnitin report), the present manuscript represents an original work with only an overlap with the existing author's publications. The first part (Chapters 1-4) is a pedagogical introduction to his field of expertise, ellipsometry and magneto-optics, with an extensive reference to literature; it is derived from a book chapter that Jan Mistrík wrote and illustrated with some examples based on his own carrier. The second part is a brief review of his personal contribution to the field; it is then deepened by the attached articles.

Since his PhD thesis (“Etudes des propriétés physiques par spectroscopie magnéto-optique de couches minces d'oxydes magnétiques préparées par dépôt laser pulsé“ from Versailles University, France), Jan Mistrík developed his scientific research on the use of optical and magneto-optical spectroscopic ellipsometry for the characterization of (nano)materials. The moto of his manuscript is the use of light polarization as a probe of matter.

After an interesting historical review about the field, Chapter 1 deals with general reminders about light polarization and ends-up with the definition of the angles used later on to characterize the polarization ellipse in ellipsometry and magneto-optics.

In the next chapter, Jan Mistrík deals with light-matter interaction. The question of light propagation is handled first in terms of the general linear constitutive equations involving the dielectric tensor of the medium. In the simplest case, it is a scalar quantity. However, a material can be intrinsically anisotropic leading to birefringence or dichroism. The problem becomes subtler, even for an isotropic optical medium, when a magnetic field change the symmetry of the system. This is the domain of magneto-optics covered by Jan Mistrík during his carrier. Anti-symmetric off-diagonal elements emerge in the dielectric tensor through an expansion up to second order in magnetic field. Depending on the direction of the magnetic field relative to the wave vector, they lead to the Faraday effect in transmission (circular magnetic birefringence and dichroism) when parallel or Voigt effect (linear magnetic birefringence and dichroism) when perpendicular. After a reminder about the usual long wavelength approximation of optics that allows ignoring non-local effects, the Kramers-Kronig relations based on the causality principle are introduced. They are central in ellipsometry to extract/check the complex optical constants. Follows the classical physical interpretation of the optical constants in terms of Lorentz oscillator and Drude models used to describe interbands and intraband excitations. They are at the heart of the parametrization of the dielectric function used in the analysis of ellipsometry measurements. The link is then made to the quantum picture of electronic transitions *i.e.* oscillator strengths, lifetimes, dipole matrix elements and the concepts of direct/indirect transitions and of band gap. The same description, but for magneto-optical constants, is then introduced; the polarization is not anymore colinear with the electric field because of the magnetic Lorentz force. On a quantum point of view, the origin of the phenomenon is the spin-orbit interaction. The chapter concludes with a short section on *ab initio* calculations without entering too much into the theoretical difficulties to determine accurately excited states and therefore optical constants. Here a better overview of theory limitation would have been welcome to contextualize the interest of the accurate determination of (magneto)optical constants for theoretical calculations.

Ellipsometry, described in details in chapter 3, measures the change of polarization state of light by a non-normal reflection on a sample surface. It is an invaluable non-destructive technique from which optical constants and morphological information can be obtained. The ellipsometric parameters, introduced first in the case of an isotropic sample, are then generalized to the anisotropic case and the mixing of s-and p-wave via the Jones vector. Follows a general description of the principle a null ellipsometry setup. The remainder of the chapter is devoted to the main concepts and applications of ellipsometry to samples of increasing complexity: (i) a bulk material, (ii) a single layer, (iii) multilayers and (iv) linear grating. Each section is carefully illustrated by examples from Jan Mistrík's own research. Based on the Fresnel equations, an inverse analytical formula can be obtained to derive directly the dielectric constants of a bulk isotropic material from ellipsometric angles. As pointed by the applicant, the role of the Beilby damaged surface layer should of course be kept in mind during measurements. The case of an anisotropic medium is more involved and simplifies only for specific orientations of the crystallographic axis and of the incident plane. Normal reflectivity measurement combined with Kramers-Kronig relations can also be used to obtain dielectric constants; but this requires the largest possible wavelength range as illustrated on $PbZr_xTi_{1-x}O_3$ with synchrotron measurements. Due to interference fringes (if absorption is low), spectroscopic ellipsometry on a single layer allows to derive both its optical constants but also its thickness. But this is at the expense of a more complex modelling based on non-linear fitting that requires an educated parametrization of optical constants, Kramers-Kronig consistency checks, measurements at several angles and complementary transmittance/reflectance spectra to achieve reliable fits. The case is illustrated with an ideal chalcogenide layer and defective silica films studies by the candidate. In the light of the present report, Jan Mistrík masters perfectly this art of fitting! Nevertheless, the pitfalls of such an analysis could have been more detailed for an unexperienced user, in particular the guidelines for the choice of parametrization and the systematic analysis of cross-correlations between parameters. Next, the case of multilayers requires the use of matrix calculations to account for transmission/reflection at each interface and wave propagation in each layer. The case is illustrated with a work on seeded CVD diamond growth that implied the test of several sample models. The treatment of inhomogeneous layers, composite materials and layer roughness requires often the use of effective medium approximations. But their validity and limitations could have been discussed. In the case of these complex systems, Jan Mistrík underlines rightly here the requirement of the coupling of ellipsometry with complementary techniques. At last, the chapter concludes with scatterometry *i.e.* the extension of ellipsometry to periodically nanostructured materials through the measurement of the zero-order diffraction peak. Here, the data analysis to extract morphological information is much more involved and implies specific and less common simulation tools that Jan Mistrík masters. The case is illustrated with linear Ni gratings for which the non-invasive ellipsometry turned out to be sensitive to oxidation layer at variance to other techniques such as atomic force microscopy.

Chapter 4 is devoted to magneto-optical effects in reflection, a field to which Jan Mistrík brought an interesting and original contribution. It starts with a general description of the Kerr effect in polar, longitudinal and transversal configurations, of the magneto-optical angles and of the used experimental setup based on modulation techniques to achieve the high accuracy required to measure small angles. Following the same spirit as in the previous chapter, Jan Mistrík treats systems of increasing complexity: (i) single interface, (ii) single layer (iii) multilayer and (iv) linear grating. Again, on a single interface, provided that the refraction index known, off-diagonal elements of the dielectric tensor can be analytically linked to polar Kerr rotation and ellipticitiy measured at normal incidence. The case is illustrated by a measurement on $NiFe_2O_4$ for which surface damage could bias the conclusion. Linear and quadratic magneto-optical contributions are then discussed in the case of in-plane magnetization and illustrated in the case of Fe. Then, in the case of polar Ker effect on a single layer, the role of thickness and absorption is pointed out in the relative contributions of light reflection at the upper interface and of propagation. The point is illustrated with films of $NiFe_2O_4$ and then of $SmFeO_3$. For the latter material, Faraday rotation could be used to explore the relationship between synthesis conditions, film quality and magnetic properties. In the case of Fe_2O_3/NiO multilayers, magneto-optical measurements turned out to be more sensitivity to interdiffusion and formation of interfacial $NiFe_2O_4$ than spectroscopic ellipsometry. The chapter concludes with a MOKE analysis of a permalloy grating combining zero and first diffraction peak measurements. Data analysis turned out to be sensitive to oxidation and edges effects that escape to standard measurements, but at the expense of quite involved simulations. As demonstrated by Jan Mistrík , even if the field of magneto-optics is less mature than regular ellipsometry, it can bring decisive information about the magnetic arrangement of the sample.

Chapter 5 to 7 gather quick summaries of the contributions of Jan Mistrík to the field of ellipsometry and magneto-optics. He smartly grouped them into general topics which echo the concepts developed in the previous chapters: (i) determination of optical and magneto-optical constants, (ii) characterization of nanostructures (films, multilayers, grating) and (iii) theoretical approaches. This section combined with the portfolio of selected publications demonstrates the extent and diversity of the topics covered by the applicant (growth and doping, surface plasmon, magnetic ordering, interdiffusion, etc…) for various materials ranging from metal, to oxide and polymers. Each time, he tried to pinpoint the role of ellipsometry in the problem at hand. Most of the presented works result from numerous external academic collaborations. He also did high-level service provision for several companies in Japan and Czech Republic. Nevertheless, beyond the crucial role of ellipsometry technique in the questions at hand, the own scientific topic of the candidate in terms of material science, solid state physics or nanoscience is hard to figure out.

The manuscript ends up with a brief description of a few general perspectives that are more related to the field itself and not to the applicant. I would have expected a more personal and developed description of his own projects in the long term.

To sum up, Jan Mistrík proposed an habilitation thesis centred on his technique of predilection. The scientific report, the attached articles as well as the publication record (64 publications, h-factor of 16) demonstrate the high quality and impact of the scientific research conducted by Jan Mistrík since his PhD. In addition, the complete and clear high-level overview of the first part of the document testifies of his pedagogical skills but also of his scientific rigor. I really appreciated the effort put by the candidate in this part! During his carrier, Jan Mistrík covered a wealth of scientific topics in the field of (nano)materials. His recognized know-how in ellipsometry and magneto-optics and its analysis appear through the numerous collaborations he developed across the world. **In my opinion, he deserves undoubtfully the habilitation degree from Charles University and I give without restrictions the green light for the oral defence.**

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