



**UNIVERSITÉ DE LIÈGE**

**Faculté des sciences**

# *Ab-initio* calculation of spin dependent transport quantities in disordered materials

**Défense de Thèse pour l'obtention du titre de Docteur en Sciences**

par

**Marco DI GENNARO**

Membres du jury:

Prof. Matthieu Verstraete, promoteur
Prof. Philppe Ghosez, président
Prof. Gustav Bihlmayer
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Prof. Georg Madsen
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**Septembre 2015**

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# Abstract

The study of mutual interaction between microscopic excitations in Solid State Physics opened the way to an impressive technology development. Over the time lapse of a couple of decades, scientists managed to improve the efficiency and capacity of spin-based electronic devices to a level able to overcome Moore's law for traditional electronics. Often, these acheivements have been predicted theoretically before their experimental establishment.
In this Thesis, I present a theoretical method to calculate macroscopic transport quantities systematically from first principles. We use *ab-initio* Density Functional Theory to calculate electronic ground state properties. We consider vibrational excitation within perturbation theory and we include anharmonic terms within quasi harmonic approximation. We consider the special cases of spin-polarized materials, spin-orbit coupled materials and disordered materials.
A theory to introduce temperature corrections to the calculation of magnetic exchange interactions is also presented. Magnetic ground state properties are studied within the *ab-initio* Korringa-Kohn-Rostoker method, and magnon-phonon coupling is estimated within a frozen-phonon, frozen-magnon approach. This correction gives an estimation of the weight of magnon-phonon coupling effect which is normally neglected in well established first-principle methods for the calculation of magnetic properites of materials such as Mean Field Approximation and Atomistic Spin Dynamics. Results for a set of materials which are interesting for Spintronics and Spin-Caloritronics applications are presented.
The physics of the interface between a spin-polarized material and a heavy-metal is also analyzed, and the magnetic proximity effects arising in this kind of systems due to the Dzyaloshinskii-Moriya interaction are qualitatively presented.

# Résumé

En physique de la matière condensée, l'étude des interactions entre excitations microscopiques a ouvert la voie à d'impressionnants développements technologiques. Durant ces quelques dernières décennies, les chercheurs sont parvenus à améliorer l'efficacité des dispositifs électroniques basés sur le spin. Ces découvertes ont permis à l'industrie de l'électronique de countorner la loi de Moore qui prédisait l'évolution des performances de nos ordinateurs. Les découvertes qui ont permis ces améliorations ont souvent été prédites théoriquement avant d'avoir putre réalisées expérimentalement. Dans cette thèse, Je présente une méthode théorique permettant de calculer les propriétés de transport macroscopique à partir des premiers principes. Nous utilisons la théorie de la fonctionnelle densité au niveau ab-initio pour calculer les propriétés électroniques de l'état fondamental des cristaux étudiés lors de cette thèse. Les propriétés des excitations vibrationnelles harmoniques sont établies grâce à la théorie de la perturbation et la partie anharmonique de l'excitation a été déterminée sur base de l'approximation quasi harmonique. Les structures considérées ici sont des matériaux polarisés en spin, des matériaux comprenant un couplage spin-orbit et des matériaux désordonnés. Ici sera également présenté une théorie permettant d'introduire les effets de la température au calcul des interactions d'échanges magnétiques sous forme de corrections. Les propriétés magnétiques de l'état fondamental sont étudiées avec la méthode ab-inition Korringa-Kohn-Rostoker, et le couplage magnon-phonon est déterminé en se basant sur une approche de frozen-phonon et frozen-magnon. Cette approche permet d'estimer l'importance de ce couplage qui est habituellement négligé dans les méthodes habituelles telles que Mean Field Approximation et Atomistic spin dynamics. Les résultats présentés ici concernent des matériaux aux propriétés très interessantes pour des applications en spintronic et spin-caloritronic. Les propriétés physiques de l'interface entre un matériau polarisé en spin et un métal lourd sont aussi analysées, et une analyse qualitative des effets de proximité magnétique apparaissant dans ce type de système et relative à l'intéraction Dzyaloshinskii-Moriya a également été réalisée.

# Contents

# Preface

In this Thesis I present the results I have achieved throughout my Ph.D. at the University of Liège which I started on March $15^{th}$, 2011.
Two main research lines have been developed throughout the past four years. The first one regards the role dynamical stability of the high pressure phases of Calcium within the Density Functional Theory methods and the effect that finite temperature has on phonon frequencies. My results on were published on *Physical Review Letters* **111**, 025503, 2013 [**?** ] and will not be treated in this Thesis.
This Thesis is entirely devoted to the results I obtained regarding the F.N.R.S.-F.R.I.A. project "Ab initio study of the Spin Seebeck Effect in metallic alloys" which I presented in October $21^{st}$, 2011, to the Education Ministry of the Belgian French community and which was approved on December $15^{th}$, 2011.
The Spin Seebeck Effect is a physical effect discovered in 2008, which attracted the curiasity of the Solid State Physics community due to its asthonishing properties. The interest of the scientific community for the Spin Seebeck effect was initially so large that an entirely new research field has been introduced after it, i.e. the Spin-Caloritronics, whose aim is the study of the mutual interactions of magnetic and temperature excitations in solids. Actually the Spin Seebeck Effect revealed to be so complicated that at this stage, a microscopic theory is still missing.
The Thesis is organized as follows. A short and colloquial introduction is given. Chapter one presents three field of research in Solid State Physics: Thermoelectrics, Spintronics and Spin-Caloritronics. Each of them studies the coupling of different excitations (electronic charge and thermal excitations, electronic charge and electronic spin, electronic spin and thermal excitations respectively) and how these coupling influences or generates new physical properties. The three subjects are huge subjects if taken alone, so I tried to mention only theit most important features, in function of what is done in the rest of the Thesis.
Chapter two introduces the theoretical workhorses and basis formalism and lexicon for the rest of the Thesis: Electronic Structure, Density Functional Theory, Empirical Magnetic Models, Atomistic Spin Dynamics, Phonons, Magnons etc.
In Chapter three, the Semiclassical Theory of Transport is briefly introduced and the Lowest Order Variational Approximation to the Boltzmann transport equation as introduced by P.B. Allen in the 70's. The Relaxation Time Approximation to the Boltzmann equation is introduced as well. Explicit relations for resistivity, Seebeck coefficient and thermal conductivity are derived and calculated for Copper.
In chapter four, I apply systematically this method to a set of chosen materials which are interesting for Spintronics and Spin-Caloritronics applications. I show the virtues and the limits of the Lowest Order Variational Approximation compared to the Relaxation Time Approximation.
Chapter five presents a quantitative *ab-initio* calculation of temperature dependent exchange integrals in spin polarized materials commonly used in Spintronics and Spin-Caloritronics devices. Ground state exchange integrals calculations and *ab-initio* thermal vibration of atoms in the lattice

are considered, and the temperature dependent exchange are derived within a frozen-phonon frozen-magnon approach. Modifications to the theoretical Curie termperature calculations from Mean Field Approximation and Magnon Band Structure are presented.
Finally, Chapter 6 contains a discussion of the proximity magnetic effects which can arise at the Ferromagnetic-Heavy metal interfaces, which present peculiar physical properties and represent the base of many Spintronics and Spin-Caloritronics devices.
All the results presented in this Thesis are original and carried out mainly in the Nanomat group of the Physics Department of the University of Liège.