Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes the PhD subject and supervisor proposed by the French Polytech network of 14 university engineering schools. Please contact the PhD supervisor by email or Skype for further information regarding your application.

Supervisor information	
Family name	SILLY
First name	Gilles
Email	Gilles.silly@umontpellier.fr
Web reference	https://www.icgm.fr/en/chv-homepage
Lab name	Institut Charles Gerhardt de Montpellier
Lab web site	https://www.icgm.fr/
Polytech name	Polytech Montpellier
University name	Université de Montpellier
Country	France

PhD information	
Title	125Te NMR and ab initio calculations in Te materials
Main topics regards to CSC list (3 topics at maximum)	Information, storage and sensor materials
Required skills in science and	General knowledge in physics, Quantum Mechanics,

engineering	Chemistry andMaterials science.

Subject description (two pages maximum)

Tellurium containing materials are used in many technological applications including conversion energy thermoelectric devices [i], optical or electrical information storage devices [ii] and IR optical fibers or waveguides [iii], so they represent a family of materials of huge interest in the current societal challenges. Development of new materials always implies an accurate modeling of the system at the atomic level. This project positions itself far ahead of any system design modeling and it focuses on accurate modeling of tellurium chemical bonding which will be assessed by Nuclear Magnetic Resonance (NMR) spectroscopy measurements. This technique is extremely sensitive to the electronic configuration in the vicinity of the nucleus of interest which is here ^{125}Te.

The oxidation state of Tellurium can vary a lot. Te chemical bonds are very versatile leading to a large variety of materials: tellurides, tellurites, ... Even in a given family, for example tellurides (of major interest for applications), a rich variety of chemical bonding, ranging from strongly covalent to semi-metallic or resonant bonding, can be found. An accurate description of tellurium bonding can be considered as a fundamental first step before approaching any system of interest for real applications. Available methods for calculation of electronic structure and NMR parameters in solids are based on Density Functional Theory (DFT). Among those, augmented plane-waves (APW) implemented in the WIEN2K code [iv], offers a full potential and all electron approach, which is essential for NMR parameter calculation when dealing with metallic systems [v] or heavier elements.

This motivates the project to focus on Te bonding, which is rather complex, monitored via coupled NMR parameter measurements and calculations in selected materials of interest (Phase Change Materials …). The aim of the project is to i) develop specific tools combining experimental NMR data and ab initio calculation able to measure and compute NMR shifts and shielding for model Te-containing materials as precisely as possible and ii) use the resulting know-how to investigate the structure of more complex PCM materials (relevant to industrial applications) in order to establish structure/properties relationships.

The computational part of the project will be performed within framework of Density Functional Theory (DFT) implemented in the WIEN2k code [www.wien2k.at] including the recently developed NMR package [vi]. WIEN2k solves the Kohn-Sham equations using an augmented plane-wave basis (APW), a full potential and considering all electrons. The NMR package for the orbital part of the shielding tensor implements a linear response formalism in which the induced current is computed as a first order response to an external magnetic field and integrated according to Biot-Savarts law. The implementation follows the WIEN2k and APW approach and it calculates the induced current without any shape approximation. The code has been proven reliable and accurate for a wide range of nuclei and compounds.

From the NMR point of view ^{125}Te is a non-straightforward nucleus because of its low natural abundance leading to small sensitivity and extremely large NMR linewidths in most of the compounds using standard techniques. Nevertheless recent experimental methods such as WURST-CPMG pulse sequence [vii] allow recording a spectrum over a 1.25MHz range in one shot and in reasonable delays. This technique combines amplitude and phase modulated pulses allowing frequency sweeping during the pulses with CPMG technique based on echoes which allow to record few tens of free induction decay signals (instead of one) in a single scan. More recent 2D (MAT-PASS and pj-MAT) techniques even allow obtaining high resolution map in crystallized and disordered systems [viii,ix].

In the project, first a series of relevant crystallized model systems will be chosen on the basis of their structure in such a way that the whole range of expected 125Te NMR shift could be explored. The materials will be synthesized and NMR measurements will be carried out within the first 2 years. The second period should be devoted to interpretation of NMR spectra of model systems and more complex systems including some degree of disorder such as vacancies or doping. The last year will be used to focus on materials of interest for applications such as Phase Change Materials of the Ge-Sb-Te ternary, GeTe:GeSe pseudo binary systems enlarged to thermoelectric materials [18] or derived from As2Te3 for instance.

---

[i]. « Complex thermoelectric materials », G. J. Snyder, E. S. Toberer, Nature Mater. (2008) 7, 105 (doi:10.1038/nmat2090)

[ii]. « Phase Change Materials and Their Application to Nonvolatile Memories », S. Raoux, W. Wełnic, D. Ielmini, Chem. Rev. (2010) 110, 240–267 (doi: 10.1021/cr900040x)

[iii]. « C.Vigreux, E. Barthelemy, L. Bastard, J. E. Broquin, M. Barillot, S. Menard, G. Parent, and A. Pradel, Opt. Lett. (2011), 36(15), 2922 (doi.org/10.1364/OL.36.002922); P. Lucas, Z. Y. Yang, M. K. Fah, T. Luo, S. B. Jiang, C. Boussard-Pledel, M. L. Anne, and B. Bureau, Opt. Mater. Express (2013) 3, 1049. (doi.org/10.1364/OME.3.001049)

[iv]. « WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Tech. Universität Wien, Austria, 2001). P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J.Luitz, http://www.wien2k.at

[v]. « NMR Shielding in Metals Using the Augmented Plane Wave Method », R.Laskowski and P.Blaha, J. Phys. Chem. C (2015) 119, 19390−19396 (doi:10.1021/acs.jpcc.5b05947)

[vi]. « Calculations of NMR chemical shifts with APW-based », R. Laskowski, P. Blaha, Physical Review B (2012) 85, 035132. (doi:10.1103/PhysRevB.85.035132). « Calculating NMR chemical shifts using the augmented plane-wave method », R. Laskowski, P. Blaha, Physical Review B (2014) 89, 014402. (doi:10.1103/PhysRevB.89.014402). « Assessment of DFT functionals with NMR chemical shifts », R. Laskowski, P. Blaha, F. Tran., Physical Review B, 87 (2013), 195130. (doi:10.1103/PhysRevB.87.195130). « Origin of NMR shielding in fluorides", R. Laskowski, P. Blaha, Physical Review B, 85 (2012), S. 245117. (doi:10.1103/PhysRevB.85.245117)

[vii]. « QCPMG Using Adiabatic Pulses for Faster Acquisition of Ultra-Wideline NMR Spectra. », L. A. O'Dell,; R. W. Schurko, Chem. Phys. Lett. (2008) 464, 97−102. (doi.org/10.1016/j.cplett.2008.08.095)

[viii]. « MATPASS/CPMG: A sensitivity enhanced magic-angle spinning sideband separation experiment for disordered solids », I. Hung, T. Edwards, S. Sen, Z. Gan, JMR (2012) 221, 103–109 (doi.org/10.1016/j.jmr.2012.05.013)

[ix]. « Tellurium Speciation, Connectivity, and Chemical Order in As_xTe_{100-x} Glasses: Results from Two-Dimensional ^{125}Te NMR Spectroscopy », D. C. Kaseman, I. Hung, K. Lee, K. Kovnir, Z. Gan, B. Aitken, S. Sen, J. Phys. Chem. B 2015, 119, 2081−2088 (doi: 10.1021/jp5123618)