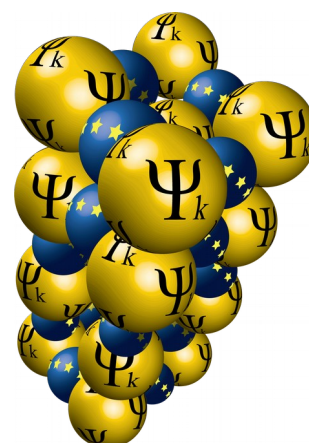




Thermoelectric Materials: From Theoretical Design to Industrial Application

Tyndall National Institute, Cork, Ireland

July 3-6, 2017



Foreword

This workshop will highlight recent developments in the theory of thermoelectric materials and explore how they can inform experimental developments and industrial applications of these materials. Our aim is to provide a forum for interactions between leading scientists working on various aspects of thermoelectric materials, from fundamental theory and computational methods, through materials growth and characterization to industrial application. Each has much to learn from the others' areas of interest: those involved in the experimental development of new materials or in their industrial application will learn about new capabilities emerging in the area of theoretical materials design; theorists will be challenged to translate their understanding of thermoelectric phenomena into more intuitive guiding principles for the experimental community.

There is a strong emphasis on the European scientific and industrial communities and possibilities for improved cooperation at European level but invited speakers will also come from the USA. The workshop is supported by Science Foundation Ireland through its Catalyst Award scheme and aims to promote the development of coherent Europe-wide initiatives that will connect basic science with its applications and enhance the societal impact of the research supported by the Foundation in Ireland. The Catalyst Award provided travel and accommodation support and running costs for invited speakers. The workshop is also supported by the Psi-k network, dedicated to the advancement of first-principles computational materials science. Psi-k provided accommodation and running costs for PhD students who attend the workshop. We are very grateful to Science Foundation Ireland and Psi-k for their generous support.

We hope that you will enjoy the workshop and your visit to Cork and Ireland!

Ivana Savić, Stephen Fahy, Kafil Razeeb, Jorge Kohanoff, Myrta Gruening, Tchavdar Todorov, and Yaniv Gelbstein

Scientific Committee

Ivana Savić, Stephen Fahy, and Kafil Razeeb
Tyndall National Institute, Cork, Ireland

Jorge Kohanoff, Myrta Gruening, and Tchavdar Todorov
Queen's University Belfast, UK

Yaniv Gelbstein
Ben-Gurion University of the Negev, Beer-Sheva, Israel

Local organizers

Ivana Savić
Stephen Fahy
Danny Denton

Programme overview

Registration will take place inside the front main entrance to Tyndall National Institute on Monday July 3rd, 2017 from 15:45, followed by the plenary session starting at 16:30 in room B.0.17-1.

Tuesday July 4th and 5th, 2017 will include oral sessions with invited and contributed speakers starting at 8:30 in room B.0.17-1. Refreshments during coffee breaks will be served in Atrium B. Lunch breaks will take place in the Tyndall canteen.

Slots for plenary talks are 35 minutes for presentation, and 10 minutes for Q&A. Slots for invited talks are 30 minutes for presentation, and 10 minutes for Q&A. Slots for contributed talks are 15 minutes for presentation, and 5 minutes for Q&A.

Poster session will take place on Tuesday July 4th, 2017 at Atrium C. Posters should be prepared in A0 format.

Thursday July 6th, 2017 will include open discussion about future directions in the field, and possibilities for EU and international collaborations, starting at 9:00 in room B.0.17-1.

Directions from Cork Airport to Cork City Centre

Bus connections to/from the airport are provided by Bus Eireann, route No 226 to Cork Bus Station. The bus timetable is available at <http://www.buseireann.ie/timetables/1474644447-226.pdf>

Accommodation is within walking distance from Cork Bus Station (Garnish House-25 minutes, Lancaster Lodge-20 minutes, Maldron-15 minutes, River Lee-20 minutes), see the map on the next page.

A taxi journey from Cork Airport to Accommodation (Garnish House, Lancaster Lodge, Maldron or River Lee) will take 10-20 minutes and will cost about €12-18.

Taxi companies

Cork Taxi Co-op: +353 (0)21 427 2222

ABC Taxis: +353 (0)21 496 1961

Directions to Tyndall National Institute

The map of Cork City Centre including Tyndall National Institute, Garnish House, Lancaster Lodge, Maldron and River Lee Hotels is given on the next page.

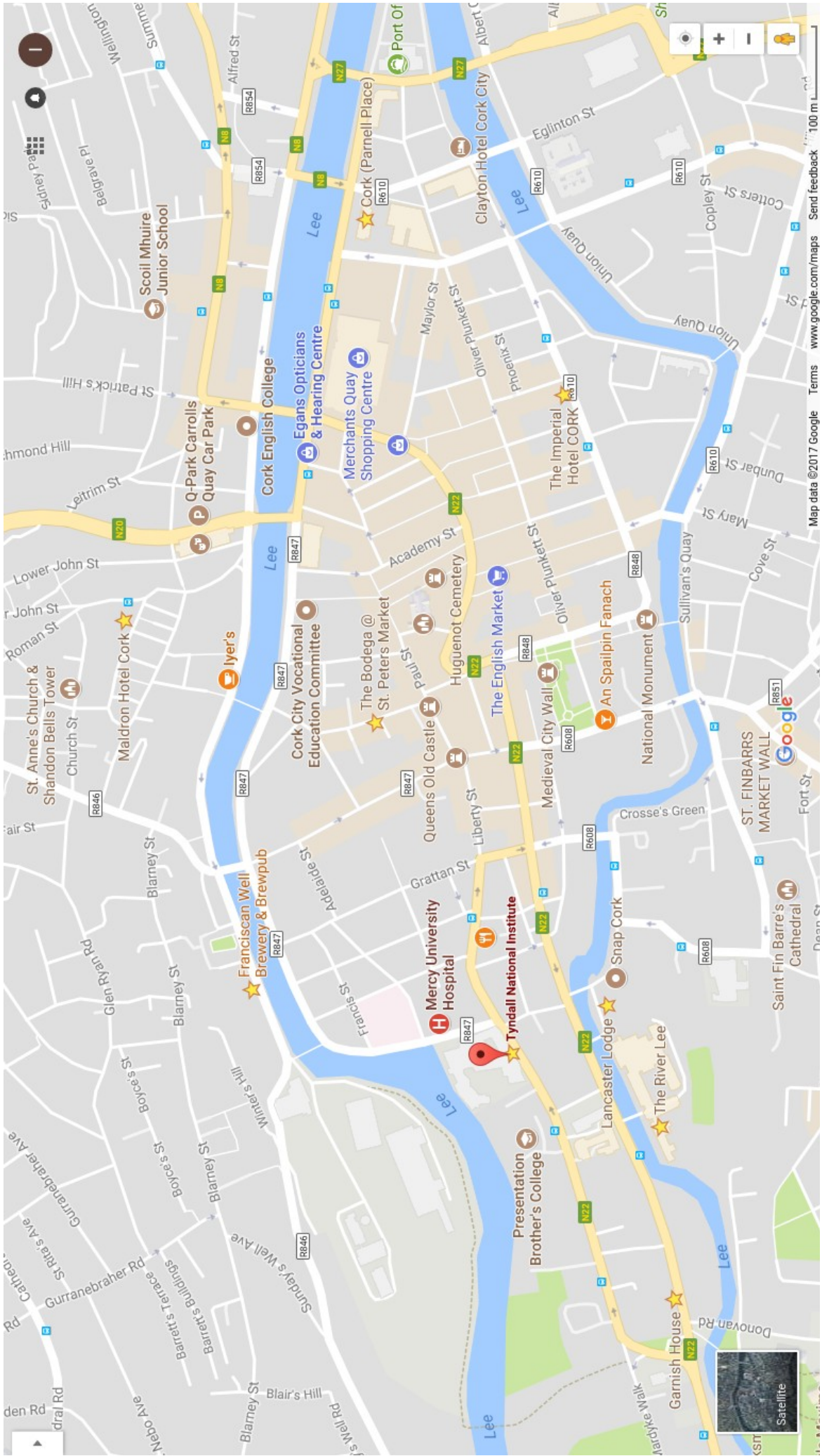
Directions to restaurants and pubs for evening gatherings

The map of Cork City Centre including Bodega@St. Peters Market, Imperial Hotel and Franciscan Well Brewery and Brewpub is given on the next page. The individual addresses are:

Bodega@St. Peters Market, 44-45 Cornmarket Street, Centre, Cork

South's Bar, Imperial Hotel Cork, South Mall, Cork

Franciscan Well Brewery and Brewpub, 14 North Mall, Sunday's Well, Cork



Map data ©2017 Google

Terms

www.google.com/maps

Send feedback

100 m

Satellite

Programme

Day 1: Monday July 3rd, 2017

15:45-16:15 Registration

16:15-16:30 Welcome

Plenary Session: New Material Design Concepts

Chair: Anke Weidenkaff, University of Stuttgart, Germany

16:30-17:15 **G. Jeffrey Snyder**, Northwestern University, USA
Fermi Surface Complexity Factor for Thermoelectric Materials

17:15-18:00 **David Singh**, University of Missouri, USA
Methods for Identifying New High Performance Thermoelectric Materials

Social Evening

19:30 Dinner at Bodega

Day 2: Tuesday July 4th, 2017

8:50-9:10 Registration

Session 1: Industrial Applications

Chair: Devendraprakash Gautam, Tyndall National Institute, Ireland

9:10-9:50 **Albert O'Grady**, Analog Devices, Ireland
Industrial Applications for Thermoelectric Energy Harvesting

9:50-10:30 **Ryan Enright**, Nokia Bell Labs, Ireland
Thermally Integrated Photonics Systems

Coffee Break

10:30-11:00

Session 2: Thermoelectric Devices

Chair: Ryan Enright, Nokia Bell Labs, Ireland

11:00-11:20 **Devendraprakash Gautam**, Tyndall National Institute, Ireland
Enhanced Seebeck Coefficient of Electroplated p-type $(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Te}_3$ thin films by Te Encapsulation

11:20-11:40 **Maria Ibáñez**, ETH Zurich, Switzerland
Bottom-up Engineering of Thermoelectric Nanomaterials and Devices from
Solution-Processed Nanoparticles

11:40-12:00 **Bruno Lorenzi**, University of Milano Bicocca, Italy
From Theoretical Modeling to Lab Testing, a Way towards the Development of
Optimized and Cost Effective Hybrid Thermoelectric-Photovoltaic Devices

Lunch Break

12:00-13:30

Session 3: IV-VI and Related Materials

Chair: G. Jeffrey Snyder, Northwestern University, USA

13:30-14:10 **Bo Brummerstedt Iversen**, Aarhus University, Denmark
Structural Thermoelectrics

14:10-14:50 **Matthieu J. Verstraete**, University of Liege, Belgium
Ab Initio Phonon Limited Transport

14:50-15:30 **Yaniv Gelbstein**, Ben Gurion University, Israel
Thermoelectric Efficiency of IV-VI and V₂-VI₃ Materials Driven near Phase
Transitions

Coffee Break

15:30-16:00

Session 4: Thermal Conductivity Modelling

Chair: Matthieu J. Verstraete, University of Liege, Belgium

16:00-16:40 **Christian Carbogno**, Fritz-Haber Institute Berlin, Germany
Thermal Conductivities in Solids from First Principles: Accurate Computations and
Qualitative Insights

16:40-17:20 **Olle Hellman**, California Institute of Technology, USA
Temperature Dependent Vibrational Properties of Thermoelectric Materials

17:20-17:40 **Ivana Savić**, Tyndall National Institute, Ireland
Lattice Thermal Conductivity of PbTe Materials Driven near Ferroelectric Phase
Transition

Poster Session

- 17:40-18:40 **Perla Wahnou**, Universidad Politecnica de Madrid, Spain
Theoretical Calculation of Electronic and Thermoelectric Properties of Bi and Sn doped-Cu₃SbSe₄ from First Principles
- 17:40-18:40 **Simon Corbett**, Trinity College Dublin, Ireland
Characterisation of Thermoelectric Devices with CCD – Thermoreflectance techniques
- 17:40-18:40 **Daniela Galliani**, University of Milano Bicocca, Italy
Thermoelectric Properties of Vapour Phase Polymerized Poly(3,4 Ethylenedioxythiophene) -Trifluoromethanesulfonate (VPP PEDOT:Tf): a Study on a Highly Performing Conductive Polymer
- 17:40-18:40 **Alessio Campo**, University of Basel, Switzerland
Semiconductor Nanowires as Efficient Thermoelectric Nanomaterials
- 17:40-18:40 **Neil M. Wight**, Heriot-Watt University, Edinburgh, UK
A Universal Method for Thermal Conductivity Measurements on Micro-/Nano-Films With and Without Substrates using Micro-Raman Spectroscopy
- 17:40-18:40 **Swatchith Lal**, Tyndall National Institute, Ireland
Optimization of Electrodeposited Bi₂Te₃-Based Thin Films for Realization of Thermoelectric Energy Harvester
- 17:40-18:40 **Javier Fernández Troncoso**, Queen's University Belfast, UK
Thermal Conductivity of PbTe from Classical Molecular Dynamics Simulations
- 17:40-18:40 **Maria Troppenz**, Humboldt University Berlin, Germany
Finite-Temperature Properties of the Thermoelectric Clathrate Ba₈Al_xSi_{46-x}
- 17:40-18:40 **Djordje Dangić**, Tyndall National Institute, Ireland
Thermal Expansion of Pb_{1-x}Ge_xTe Alloys from First Principles
- 17:40-18:40 **Jiang Cao**, Tyndall National Institute, Ireland
Effect of Electron-Phonon Scattering on Thermoelectric Figure-of-Merit
- 17:40-18:40 **Ronan Murphy**, Tyndall National Institute, Ireland
Reducing the Thermal Conductivity by Driving PbTe to a Phase Transition via Strain and/or Alloying

Conference Dinner

- 19:45 Dinner at South's Bar, Imperial Hotel

Day 3, Wednesday July 5th, 2017

Session 1: Tellurides

Chair: Yaniv Gelbstein, Ben Gurion University, Israel

8:30-9:10 **Juri Grin**, Max Plank Institute Dresden, Germany
Substitutional Behavior of Lead Telluride

9:10-9:50 **Oliver Oeckler**, University of Leipzig, Germany
Crystallography of Thermoelectric Tellurides

9:50-10:10 **Pavel Korotaev**, Dukhow Research Institute for Automatics, Moscow, Russia
Supercell Modeling of Na and TI Doping of Lead Telluride

Coffee Break

10:10-10:40

Session 2: 2D and Layered Materials

Chair: Nicola Bonini, Kings College London, UK

10:40-11:20 **Troels Markussen**, QuantumWise, Denmark
First Principles Modelling of Thermo-electrics Using ATK, Comparison of Bulk and Full Device Approaches

11:20-11:40 **Graeme Cunningham**, Nokia Bell Labs, Ireland
Full Thermoelectric Characterisation of Hot Pressed Solution Processed Group VI TMD Films around Room Temperature

11:40-12:00 **Jakub D. Baran**, University of Bath, UK
Insight into Thermoelectric Properties of High-Performance Layered Oxides: A Cooperative Computational and Experimental Study

Lunch Break

12:00-13:30

Session 3: Half-Heuslers

Chair: Christian Carbogno, Fritz-Haber Institute Berlin, Germany

13:30-14:10 **Anke Weidenkaff**, University of Stuttgart, Germany
Thermoelectric Materials for the Medium- and High-Temperature Range (600 K<T<1200 K)

14:10-14:50 **Georgy Samsonidze**, Bosch, USA
Thermoelectricity by Rational Design: New Materials and Insights from First-Principles Computations of Carrier Scattering

14:50-15:30 **Ankita Katre**, CEA-Grenoble, France
Unveiling the Role of Defects in Thermal Transport: an Ab Initio Study Using AlmaBTE Code

Coffee break

15:30-16:00

Session 4: Thermoelectric Transport Modelling

Chair: David Singh, University of Missouri, USA

16:00-16:40 **Giovanni Vignale**, University of Missouri, USA
Nonequilibrium Thermal Density Functional Theory - a Microscopic Approach to Thermoelectric Transport

16:40-17:20 **Nicola Bonini**, Kings College London, UK
Thermoelectric Properties from First-Principles via the Exact Solution of the Boltzmann Transport Equation

17:20-17:40 **Phillip Murphy-Armando**, Tyndall National Institute, Ireland
Study of the Effect of the Scattering rate on the Thermopower

17:40-18:00 **Fabio Ricci**, University of Liege, Belgium
About the Electronic Properties of Fe₂VAl and Related Thermoelectric Compounds

Social Evening

19:30 Dinner at Franciscan Well

Day 4: July 6th, 2017

Session 1: Discussion

9:00-11:00 Open Discussion and Future Directions

Day 1

Monday July 3rd, 2017

Plenary Session

New Material Design Concepts

16:30-18:00

Fermi Surface Complexity Factor for Thermoelectric Materials

G. Jeffrey Snyder

Department of Materials Science and Engineering, Northwestern University

email: jeff.snyder@northwestern.edu

website: thermoelectrics.matsci.northwestern.edu

The DOS and transport effective masses are commonly used to describe electronic transport in semiconductors using a classical analogy to the kinetic theory of gasses. In thermoelectrics we often use the Seebeck coefficient to characterize the DOS mass while mobility depends inversely on the inertial or transport mass. In materials with complex electronic structures these two masses can vary significantly. For example, in many valley electronic structures such as PbTe, with N_V isolated valleys in the Fermi surface, the DOS mass can be high and inertial mass low for high thermoelectric quality factor. High valley degeneracy has been found in many high zT systems such as Bi₂Te₃, Mg₂(Si,Sn), CoSb₃ skutterudites and some Half Heuslers. In real systems the Fermi surface pockets can be anisotropic and even non-ellipsoidal, which also appears to be beneficial to the quality factor.

Using examples of real semiconductors we calculate from DFT the equivalent effective masses from the Seebeck coefficient and electrical conductivity. We find that the ratio of these different masses can be understood as the *complexity factor* which contributes to the thermoelectric quality factor and therefore zT .

1. Gibbs, Snyder et. al., *Computational Materials* **3**, 8 (2017)

Methods for Identifying New High Performance Thermoelectric Materials

David J. Singh

University of Missouri, Columbia, Missouri 65211-7010 USA

Thermoelectric devices are used for the conversion of thermal and electrical energy. Applications are enabled by high performance materials, characterized by a dimensionless figure of merit, $ZT = \sigma S^2 T / \kappa$. There is no known fundamental limit on ZT but it is a contraindicated property of matter. The challenge for theory is to find ways of overcoming this contraindication and discovering materials that exemplify those principles. In this talk I discuss electronic structure features that can be associated with high ZT as well as methods for identifying new high performance materials. Application to classes of materials and examples are presented.

This work was supported by the U.S. Department of Energy through the S3TEC Energy Frontier Research Center.

Day 2

Tuesday July 4th, 2017

Session 1

Industrial Applications

8:30-9:50

Industrial Applications for Thermoelectric Energy Harvesting

Albert O'Grady

Analog Devices Ireland, Limerick, Ireland

The focus of this presentation is on the development of a "zero-pin" sensor utilizing thermoelectric energy harvesting targeted at industrial applications. A zero-pin sensor is a self-contained solution that converts ambient energy to electrical power used to power a node, while detecting or measuring a physical property and wirelessly transmitting data to a gateway/cloud. Energy harvesting affords the opportunity to power circuits and charge, supplement and even replace batteries in systems where they are inconvenient, impractical expensive or dangerous. Machine Health Monitoring is one target application for Industrial Internet-of-Things (IIoT) where replacing reactive maintenance with a predictive maintenance strategy is pursued to reduce the cost and disruption of unplanned maintenance. A zero-pin sensor solution for this application incorporates a thermoelectric energy harvester powering a vibration monitoring sensor with a wireless interface portraying the state of health of the machine. We will focus on the customer journey and what it takes to build a self-powered sensor node. Many challenges arise as signal levels from the harvesting sensor are generally very low placing constraints on the power management device to operate at very low voltages and with extremely low iq to ensure that the power management device does not significantly load the source. An ultra low power (ULP) signal chain including accelerometers, temperature sensors, microcontroller and radio interface is imperative in making a self-powered solution feasible. This paper discusses all facets of the design including the thermoelectric energy harvester and optimizing the signal chain for ultra-low power operation.

Thermally Integrated Photonics Systems

Ryan Enright

Bell Labs Ireland, Blanchardstown Business & Tech Park, Snugborough Rd, D15 Y6NT, Ireland

Network data traffic is growing at unprecedented rates and, as a result, there are significant hardware changes occurring in the network. In particular, integrated silicon photonics has emerged as a scalable optoelectronic platform to meet the demands for increased bandwidth in communication networks across a wide range of link distances. However, integration introduces new thermal challenges to achieving the required system performance under standards-dictated ambient conditions. Here we present a thermal architecture for silicon photonics called TIPS (Thermally Integrated Photonics System) that provides thermal component building blocks to enable \gg Tb/s capacities with reduced J/bit in the smallest form factors possible with particular focus on integrated solid-state cooling.

Traditionally, temperature-sensitive photonic devices have been cooled using centimetre-scale thermoelectric modules, but this approach does not scale favourably in terms of energy consumption and footprint for highly integrated systems where thermal isolation becomes increasingly difficult using macroscopic thermoelectric modules. Our alternative approach, currently being developed for a silicon photonics platform, is to integrate thermoelectric temperature control at the device level to provide targeted cooling for individual temperature sensitive devices. We will outline both the promise and challenges of this approach and suggest research objectives in terms of thermoelectric materials and device fabrication.

Day 2

Tuesday July 4th, 2017

Session 2

Thermoelectric Devices

10:20-12:00

High Performance Thermoelectric Materials and Modules for Energy Harvesting

***N. V. Nong and L. T. Hung**

Department of Energy Conversion and Storage, Technical University of Denmark,
Roskilde 4000, Denmark

*email: ngno@dtu.dk

In this talk, our recent development of high performance thermoelectric (TE) materials and modules is presented. The highlighted results emphasize on some selective nanostructured materials include Bi-Te nanocomposites, half-Heusler alloys, and skutterudite compounds. The bulk nanostructured materials were sintered using spark plasma sintering technique, showing maximum $zT = 1.4 \div 1.6$. The stability of TE materials under various thermal cycles and large temperature gradient were investigated using a new approach by *in-situ* TEM method coupled with TE characterization. Some challenges on joining and interfacial contacts between TE materials and metallic electrodes are also discussed. A maximum conversion efficiency of 11% was demonstrated with skutterudite-based TEG module at the hot side and cold side temperatures of 600 °C and 140 °C, respectively. However, we have also observed a degradation rate of more than 4% for this module after operating for 600 h in vacuum. Further investigation revealed that Sb migration in p-skutterudite leg under large temperature gradient is the main reason for the degradation, while n-skutterudite is more stable. Finally, a new successfully demonstrated flexible TE module comprising of 100 p-n pairs for e.g. wearable power applications will also be presented.

Enhanced Seebeck Coefficient of Electroplated p-type $(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Te}_3$ thin films by Te Encapsulation

Kafil M. Razeeb and Devendraprakash Gautam

Micro-Nano Systems Centre, Tyndall National Institute, University College Cork,
Lee Maltings, Dyke Parade, Cork T12 R5CP, Ireland

Bismuth telluride and its alloys have been extensively used as material for thermoelectric power generation and cooling near room temperature applications. The potential of a material for thermoelectric applications is evaluated by a dimensionless parameter called the figure of merit, zT and is defined as

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T \quad (1)$$

where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the total thermal conductivity ($\kappa = \kappa_l + \kappa_e$, the lattice and electronic contributions respectively), and T is the absolute temperature at which the properties are measured. For an efficient thermoelectric material ZT should be as high as possible. Eq. (1) indicates to obtain efficient thermoelectric material at a particular temperature T , the quantity called the power factor, $\alpha^2 \sigma$ should be maximized while simultaneously κ should be minimized. The Seebeck coefficient enters as a squared quantity in Eq. (1) and has a huge influence on ZT .

Nanostructured materials, specifically mesoscale composites showed improved ZT values due to the reduction in thermal conductivity without reducing the electrical conductivity. However, most of these materials are being fabricated through alloying using high temperature and pressure and thereby not scalable in terms of Si based fabrication processes. The growing demand of miniaturized room temperature thermoelectric devices based on bismuth telluride alloys has led to research focused on synthesizing thin films, in particular, using electrochemical deposition. It has been observed that electroplated $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ thin film increases after annealing the film in tellurium (Te) atmosphere for 60 h, which is attributed to the improved Te content in the annealed films [*Advanced Energy Materials*, (2013), 3, 95]. However, Te is a toxic and due to its relatively moderate melting point and high vapour pressure it requires sophisticated instrumentation and high vacuum to avoid oxidation and to integrate Te in the thin films thereby making the process expensive, and industrially not up-scalable.

The objective of the present work is to synthesize electrodeposited thin films with thermoelectric properties, in particular the Seebeck coefficient similar to bulk material by achieving stoichiometric content of Te in p-type $(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Te}_3$ after annealing. We propose an innovative way where as a Te source, a thin layer of Te is encapsulated between p-type $(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Te}_3$ layers to achieve desired Te composition in the annealed films. We demonstrate that the annealed thin films with encapsulated/sandwiched Te layer has a Seebeck coefficient of about $175 \mu\text{VK}^{-1}$, which is twice higher compared to the films with no Te layer. Thus, Te encapsulation in thin films paves a new way to maintain stoichiometric Te composition in annealed films without the need for sophisticated instrumentation to handle the toxic element thereby making the annealing process facile, clean and environmental friendly. Furthermore, this encapsulation process can be adopted to augment particular elemental composition in other nanocomposite materials to enhance materials properties.

Bottom-up Engineering of Thermoelectric Nanomaterials and Devices from Solution-Processed Nanoparticles

Maria Ibáñez¹, Yu Liu², Gregorio García^{3,4}, Silvia Ortega², Yu Zhang², Doris Cadavid², Pablo Palacios^{3,5}, Perla Wahnón^{3,4}, Maksym V. Kovalenko¹, and Andreu Cabot^{2,5}

¹Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

²Catalonia Institute for Energy Research - IREC, 08930 Sant Adrià de Besòs, Barcelona, Spain

³Instituto de Energía Solar, ETSI Telecomunicación, Universidad Politécnica de Madrid, 28040, Madrid, Spain

⁴Departamento de Tecnología Fotónica y Bioingeniería, ETSI Telecomunicación, Ciudad Universitaria, s/n, 28040 Madrid, Spain

⁵Departamento de Física aplicada a las Ingenierías Aeronáutica y Naval. ETSI Aeronáutica y del Espacio, Pz. Cardenal Cisneros, 3, 28040 Madrid, Spain

⁶ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain

The conversion of thermal energy to electricity and vice versa by means of solid state thermoelectric devices is extremely appealing. However, its cost-effectiveness is seriously hampered by the relatively high production cost and low efficiency of current thermoelectric materials and devices. To overcome present challenges and enable a successful deployment of thermoelectricity in its wide application range, materials with significantly improved performance need to be designed and engineered. Nanostructuring can help in several ways to reach the very particular group of properties required to achieve high thermoelectric performances. Nanodomains inserted within a crystalline matrix can provide high charge carrier concentrations without significantly influencing their mobility, thus reaching very high electrical conductivities. Nanostructured materials containing grain boundaries efficiently scatter mid- and long-wavelength phonons, thus contributing to reduce thermal conductivity. Furthermore, nanocrystalline domains can enhance the Seebeck coefficient by modifying the density of states and/or providing type- and energy-dependent charge carrier scattering. All these potential advantages can only be reached when engineering a complex type of material, a nanocomposite, with an exquisite control over structural and chemical parameters at multiple length scales. Since current conventional nanomaterial production technologies lack such level of control, alternative strategies need to be developed and adjusted to the specifics of thermoelectricity. A particularly suitable approach to produce nanocomposites with unique level of control over their structural and compositional parameters is their bottom-up engineering from solution-processed nanoparticles. In this presentation, I will describe our progress in this field, including the synthesis of nanoparticles with precisely engineered composition and surface chemistry, their combination and consolidation into nanostructured materials, the strategies to electronically dope such materials and the attempts to fabricate thermoelectric devices using nanoparticle-based nanopowders and inks.

From Theoretical Modeling to Lab Testing, a Way towards the Development of Optimized and Cost Effective Hybrid Thermoelectric – Photovoltaic devices

B. Lorenzi

Department of Materials Science, University of Milano Bicocca,
v. R. Cozzi 55, 20125, Milano, Italy

Recently the interest around the possibility of using thermoelectric generators (TEGs) to improve the performances of photovoltaics (PV) is steeply growing. This trend is well testified by the increasing number of publications on this topic (more than 90 in the last five years) [1], and by the starting of projects and industrial activities related to this matter [2,3]. Actually considering that in PV most of the solar radiation is lost as unused heat, in principle thermoelectric heat recovery may be a viable solution. Nonetheless, the actual effectiveness of this approach is limited by the well-known temperature sensitivity of PV, and by the small efficiencies of TEGs. In particular, it has been well demonstrated how the simple combination of commercial PV and TEG devices does not lead to any convenient solution [4].

In this communication, we report on a project aiming to the development of optimized and cost effective hybrid systems. The work started from a theoretical evaluation of the device physics, supported in a second stage by a first experimental evaluation. The main results of this study showed that it is actually possible to achieve a beneficial hybridization, but only in the case of wide energy-gap PV, and for sufficiently high working temperatures [5]. These needs limit hybridization effectiveness to very few PV materials, and lead to the necessity of a proper device encapsulation (preventing radiative exchange) and a specific TEG design. After the identification of the main parameters and of the technological viable solutions to overcome the main constrains, the project is currently at its third stage, consisting in the development of an optimized prototype based on Copper Gallium Selenide solar cells, a heat mirror, and an optimized TEG. The following device characterization will give the data for a commercial/industrial evaluation of this novel class of solar systems.

1. Web of Science
2. <http://www.gla.ac.uk/research/az/suntrap/>
3. <http://www.hybridasol.com/single-post/2014/01/01/HybridaSol-received-matching-funds-from-Florida-High-Tech-Corridor-for-High-Efficiency-Low-Cost-Hybrid-Photovoltaic-Thermoelectric-Cells>
4. Narducci D, Lorenzi B. Challenges and Perspectives in Tandem Thermoelectric–Photovoltaic Solar Energy Conversion. *IEEE Trans Nanotechnol* 2016;15:348–55.
5. Lorenzi B, Acciarri M, Narducci D. Conditions for beneficial coupling of thermoelectric and photovoltaic devices. *J Mater Res* 2015;30:2663–9. doi:10.1557/jmr.2015.174.

Day 2

Tuesday July 4th, 2017

Session 3

IV-VI and Related Materials

13:30-15:30

Structural Thermoelectrics

Bo Brummerstedt Iversen

Center for Materials Crystallography, Department of Chemistry & iNANO, Aarhus University,
Denmark

The figure of merit, $zT = TS^2\sigma/\kappa$, has a central standing in thermoelectrics, and the individual components (thermopower S , electrical conductivity σ , thermal conductivity κ) relate to the transport properties of the thermoelectric material. Thus, the major part of thermoelectric science has focus on measuring and interpreting transport properties. However, all understanding of physical or chemical properties of molecular scale systems relies of precise knowledge of the atomic structure. Without knowledge of the composition and three dimensional disposition of the atoms in space, rigorous interpretation of properties is impossible. Structural techniques therefore must have a central standing in thermoelectrics.

In this talk I will discuss structural thermoelectrics exemplified through recent studies of various high performance materials PbX , GeX and SnX ($X = S, Se, Te$) as well as Cu_2Se . The crystal structures have been analyzed with the nuclear enhanced maximum entropy method (NXMEM),¹ and the thermoelectric properties relate to the detailed crystal structures.² In search for new materials, computational screening methods have been advanced, but they are no better than the structural information used to calculate the properties. Furthermore, they often lack simple measures to relate the properties to the crystal structures. A new method coined “orbital engineering” provides a simple predictive measure related to the crystal structure of layered compounds,³ and this has been used to discover the new breakthrough n-type material $Mg_3Sb_{1.5}Bi_{0.5}$.⁴ Finally, the very peculiar crystal of $CsCl$ is discussed.⁵ This crystal structure is the archetype simple cubic system taught in freshman courses all over the world. Nevertheless, the room temperature thermal conductivity is extremely low (~ 1 W/Km). Elaborate diffraction studies show that it forms highly perfect crystals with very limited structural defects. Furthermore, there is limited anharmonic motion. Do we understand all aspects of heat conduction in materials?

1. Christensen et al, *Acta Crystallogr. Sect. A* **2015**, 71, 9–19
2. (a) Kastbjerg *et al.*, *Adv. Func. Mat.* **2013**, 23, 5477-5483, (b) Christensen *et al.*, *PCCP* **2016**, 8, 15874-15883, (c) Sist *et al.*, *IUCr-J* **2016**, 3, 377-388, (d) Sist *et al.*, *Acta Crystallogr. Sect. B.* **2016**, 72, 310–316 (e) Sist *et al.*, *Chem. Eur. J.* **2017**, in press, (f) Eikeland *et al.*, *IUCr-J* **2017**, in press.
3. Zhang *et al.*, *Nature Comm.* **2016**, 7, 10892
4. Zhang *et al.*, *Nature Comm.* **2017**, 8, 13901
5. Sist *et al.*, *Angew. Chem. Intl. Ed.* **2017**, 56, 3625-3629

Ab Initio Phonon Limited Transport

Matthieu J. Verstraete

Nanomat/QMAT/CESAM, University of Liège, Liège, Belgium

e-mail: matthieu.verstraete@ulg.ac.be

We revisit the thermoelectric (TE) transport properties of two champion materials, PbTe and SnSe, using fully first principles methods. In both cases the performance of the material is due to subtle combinations of structural effects, scattering, and phase space reduction. In PbTe anharmonic effects are completely opposite to the predicted quasi-harmonic evolution of phonon frequencies and to frequently (and incorrectly) cited extrapolations of experiments. This stabilizes the material at high T, but also tends to enhance its thermal conductivity, in a non-linear manner, above 600 Kelvin. This explains why PbTe is in practice limited to room temperature applications. SnSe has recently been shown to be the most efficient TE material in bulk form. This is mainly due to a strongly enhanced carrier concentration and electrical conductivity, after going through a phase transition from 600 to 800 K. We calculate the transport coefficients as well as the defect concentrations ab initio, showing excellent agreement with experiment, and elucidating the origin of the double phase transition as well as the new charge carriers. If I have time I will show you something weird about transition metal dichalcogenides.

1. O. Hellman, IA Abrikosov, and SI Simak, PRB **84** 180301 (2011)
2. AH Romero, EGU Gross, MJ Verstraete, and O Hellman PRB **91**, 214310 (2015)
3. A Dewandre, S Bhattacharya, O Hellman, AH Romero, GKH Madsen, MJ Verstraete PRL **117** 276601 (2016)

Thermoelectric Efficiency of IV-VI and V₂-VI₃ Materials Driven near Phase Transitions

Yaniv Gelbstein

Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

In thermodynamic engines, such as thermoelectric (TE) converters, maximizing the Carnot efficiency, by applying large temperature differences, is required for maximizing the heat to electricity energy conversion. This requirement is a key factor for the desire to maximize the hot side temperature of TE converters as much as possible. Yet, practical stability considerations, such as sublimation of volatile species, composing many of the currently available TE materials, limit the hot side temperature to a certain level, depending on the specific composition. IV-VI and V₂-VI₃ like Pb_{1-x}Sn_xTe/GeTe or Bi₂Te₃ based TE compositions are known as highly efficient and stable up to a temperature of around 500°C and 300°C, respectively. Methods for optimizing the TE properties while considering stability of such materials around their maximal operation temperature will be discussed in details.

Day 2

Tuesday July 4th, 2017

Session 4

Thermal Conductivity Modelling

16:00-17:40

Thermal Conductivities in Solids from First Principles: Accurate Computations and Qualitative Insights

Christian Carbogno and Matthias Scheffler

Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany

An accurate calculation of thermal conductivities is conceptually and computationally challenging, since the assessment of vibrational heat transport in solids requires detailed knowledge of the anharmonic nuclear dynamics on macroscopic time and length scales: On the one hand, approaches based on the *Boltzmann Transport Equation* allow a computationally efficient assessment in reciprocal space by utilizing the phonon properties valid in the harmonic approximation [1]. However, these approaches fail at elevated temperatures and/or for strongly anharmonic systems, since the anharmonicity is only accounted for perturbatively. On the other hand, molecular dynamics (MD) techniques using the *Green-Kubo (GK)* formalism [2] naturally capture the full anharmonic dynamics in real space. For the exact same reason, however, they can become prohibitively costly to converge in time and size – even when numerically rapid force fields are used to approximately model the inter-atomic interactions [3].

In this work [4], we introduce a heat-flux definition and develop a formalism that seamlessly bridges the gap between these two approaches: Incoherent and strongly anharmonic effects are directly treated within a real-space *ab initio* MD, while coherent, (almost) harmonic processes are mapped into a reciprocal space representation, where they can be evaluated more efficiently. This robust, asymptotically exact scheme allows extrapolating *ab initio* GK calculations on finite time and length scales to the macroscopic limit. For both force-field and *ab initio* MD, we carefully validate and critically discuss the involved conceptual and numerical approaches by investigating heat transport in silicon and zirconia, two materials known for their particularly harmonic and anharmonic character. Eventually, we show how the developed techniques enable qualitative insights in the mechanisms and properties promoting/hindering heat transport [5].

1. D. A. Broido, *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).
2. R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Japan* **12**, 1203 (1957)
3. Y. He *et. al.*, *Phys. Chem. Chem. Phys.* **14**, 16209 (2012)
4. C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).
5. C. Carbogno *et. al.*, *Phys. Rev. B* **90**, 144109 (2014).

Temperature Dependent Vibrational Properties of Thermoelectric Materials

Olle Hellman

California Institute of Technology, Pasadena, California, USA

We present recent developments using the temperature dependent effective potential technique (TDEP) to model strongly non-harmonic materials. The method employs model Hamiltonians that explicitly depend on temperature.

I will present applications pertaining to thermal conductivity, inelastic neutron spectra and phase stabilities. In addition we investigate the non-adiabatic electron-phonon coupling and their influence on phonon spectra, and recent additions to that deal with nuclear quantum effects and efficient stochastic sampling.

This is in addition to a comprehensive introduction to the theory of phonons, anharmonicity and thermal conductivity.

Lattice Thermal Conductivity of PbTe Materials Driven Near Ferroelectric Phase Transition

Ronan Murphy^{1,2}, Éamonn Murray³, Stephen Fahy^{1,2}, and Ivana Savić¹

¹Tyndall National Institute, Cork, Ireland

²Department of Physics, University College Cork, Ireland

³Departments of Physics and Materials, Imperial College London, UK

Exploiting the fascinating properties of materials near soft mode phase transitions is an emerging concept in the quest to increase thermoelectric efficiency [1,2]. The underlying idea is that soft phonons lead to intrinsically low thermal conductivity, while possibly preserving electronic transport properties. Using first principles simulations, we show that driving PbTe near the transition from the rocksalt to a rhombohedral structure will significantly reduce its lattice thermal conductivity. We illustrate this concept by applying biaxial tensile (001) strain to both PbTe and its alloy with rocksalt PbSe, and also by alloying PbTe with rhombohedral GeTe [3].

Moreover, we investigate in detail how tuning the proximity to the soft optical mode phase transition via chemical composition affects the lattice thermal conductivity of (Pb,Ge)Te alloys [4]. We show that the anharmonic contribution to the lattice thermal conductivity is minimized at the phase transition due to the maximized acoustic-optical interaction. The interplay between anharmonicity and mass disorder shifts the conductivity minimum towards the composition at which the scattering due to mass disorder is maximized. The total lattice thermal conductivity and its anharmonic contribution vary continuously between the rocksalt and rhombohedral phases as expected for the second-order phase transition. Our results show that alloys with soft optical mode transitions are promising materials for achieving low thermal conductivity and possibly high thermoelectric efficiency.

1. D. T. Morelli, V. Jovovic, and J. P. Heremans, Phys. Rev. Lett. 101, 035901 (2008).
2. L.-D. Zhao et al, Nature 508, 373 (2014).
3. R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 93, 104304 (2016).
4. R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 95, 144302 (2017).

Day 2

Tuesday July 4th, 2017

Poster Session

17:40-18:40

Theoretical Calculation of Electronic and Thermoelectric Properties of Bi and Sn doped-Cu₃SbSe₄ from First Principles

**Gregorio García¹, Yu Liu², Silvia Ortega², Doris Cadavid^{2*}, Pablo Palacios¹, Andreu Cabot^{2*},
and Perla Wahnón¹**

¹Instituto de Energía Solar, ETSIT, Universidad Politécnica de Madrid, 28040, Madrid, Spain

²Catalonia Institute for Energy Research - IREC, 08930 Sant Adrià de Besòs, Barcelona,
Spain

*email: dcadavid@irec.cat, acabot@irec.cat

Thermoelectric materials, which can convert heat into electricity or vice versa, are attracting much attention, due to their potential applications in the energy conversion industry and providing power for electronics. In this study, we focus on Cu₃SbSe₄ compound, which has become known as potential TE material due to its excellent electrical transport properties, low thermal conductivity or cheap constituent elements. Further, doping effects with Bi and Sn the TE performance are also studied. Density Functional Theory and beyond and the Boltzmann semi-classical transport calculations are performed to determine the electronic structures and main thermoelectric transport parameters of Cu₃SbSe₄-based compounds. Comparison with experimental results provided useful information on the doping effect of TE properties and their relation with the electronic structure.

Characterisation of Thermoelectric Devices with CCD – Thermoreflectance techniques

S. Corbett, Graeme Cunningham, and D. McCloskey

School of Physics, CRANN and AMBER, Trinity College Dublin, College Green, Dublin, Ireland

In the characterisation of thermoelectric devices, complications from parasitic contacts introduce significant error and should be avoided. CCD-thermoreflectance (CCD-TR) is noncontact technique which allows sub-micron resolution thermal imaging using a standard optical microscope [1,2]. We have developed a CCD-TR setup in which the heat source can be generated using an electronic or optical excitation. We have also developed a more accurate analytical theory, which includes offsets for the DC heating and accounts for the dead time of the CCD camera. With these adjustments to the standard CCD-TR approach we have investigated temperature changes in bismuth telluride bulk and thin films with applied fields. The ultimate break-down of the thermoelectric material under high voltages is investigated. This novel approach allows spot heating to be studied rather than uniform temperature changes. The thermoelectric figure of merit can be extracted using a simple electronic measurement in conjunction with the laser induced temperature difference.

1. M Farzaneh *et al*, "CCD-based thermoreflectance microscopy: principles and applications", *J. Phys. D: Appl. Phys.*, vol. 42, 143001 (2009)
2. Peter M. Mayer, Dietrich Lürßen, Rajeev J. Ram, and Janice A. Hudgings, "Theoretical and experimental investigation of the thermal resolution and dynamic range of CCD-based thermoreflectance imaging," *J. Opt. Soc. Am. A* 24, 1156-1163 (2007)

Thermoelectric Properties of Vapour Phase Polymerized Poly(3,4-Ethylenedioxythiophene)-Trifluoromethanesulfonate (VPP PEDOT:Tf): a Study on a Highly Performing Conductive Polymer

Daniela Galliani^{1*}, Robert Brooke², Ujwala Ail², Zia Ullah Khan², Xavier Crispin²

¹Department of Material Science, University of Milano Bicocca, via R. Cozzi 55, I-20125 Milano,

Italy

²Linköping University, Department of Science and Technology, Laboratory of Organic Electronics, SE-601 74 Norrköping, Sweden

*e-mail: d.galliani1@campus.unimib.it

The possibility of using conjugated polymers (CP) as thermoelectric materials has been widely explored over the last two decades, giving rewarding results¹. Such materials are particularly attractive for room temperature application and flexible devices, but their low efficiencies in comparison with the inorganic benchmark still represent a main drawback. For this reason, several different paths have been pursued to maximise their performances²⁻⁴, by enhancing CP thermoelectric power factor ($PF=\alpha^2\sigma$, where α is the Seebeck coefficient and σ is the electrical conductivity). An appealing strategy to address this aim is focused on the increase of the polymeric crystallinity level, since it causes elevated σ and only marginally affects α value⁵. In order to obtain an highly conductive CP with a good crystallinity level, vapor phase polymerization (VPP) appears to be the best technique⁶.

This communication reports on a study on poly(3,4-ethylenedioxythiophene) (PEDOT) prepared through VPP with trifluoromethanesulfonate iron salt ($FeTf_3$) as oxidative agent, which has been proven to be particularly beneficial to the final material properties⁵. Thanks to the optimization of the recipe and post-treatment procedure, a remarkable σ value of $3095 \Omega^{-1}cm^{-1}$ has been reached, while an optimized PF value of $69 \mu WK^{-2}m^{-1}$ has been obtained thanks to a slight reduction of the polymer, i.e. dedoping. Furthermore, the progressive reduction performed on the material allowed to monitor the modification of σ and α values at different oxidation levels, giving a deeper insight on the material transport properties. The overall thermoelectric study done on this novel material will be presented, including stability investigation and dedoping performed in different conditions. The results obtained will be discussed emphasizing the synthetic and post-treatment parameters that allowed the optimization of VPP PEDOT:Tf thermoelectric features.

1. B. Russ, A. Glauzell, J. J. Urban, M. L. Chabinyk and R. A. Segalman, *Nat. Rev. Mater.*, 2016, **1**, 16050.
2. G.-H. Kim, L. Shao, K. Zhang and K. P. Pipe, *Nat Mater*, 2013, **12**, 719–723.
3. O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren and X. Crispin, *Nat. Mater.*, 2011, **10**, 429–33.
4. Y. Jin, S. Nola, K. P. Pipe and M. Shtein, *J. Appl. Phys.*, 2013, **114**.
5. M. N. Gueye, A. Carella, N. Massonnet, E. Yvenou, S. Brenet, J. Faure-Vincent, S. Pouget, F. Rieutord, H. Okuno, A. Benayad, R. Demadrille and J. P. Simonato, *Chem. Mater.*, 2016, **28**, 3462–3468.
6. R. Brooke, M. Fabretto, P. Murphy, D. Evans, P. Cottis and P. Talemi, *Prog. Mater. Sci.*, 2017, **86**, 127–146.

Semiconductor Nanowires as Efficient Thermoelectric Nanomaterials

Alessio Campo^{1*}, S. Yazji², M. Y. Swinkels³, M. De Luca¹, D. Ercolani⁴, S. Roddaro⁴, G. Abstreiter², L. Sorba⁴, E. P. A. M. Bakkers³ and I. Zardo¹

¹Departement Physik, Universität Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

²Walter Schottky Institut & Physik Department, Technische Universität München, D-85748 Garching, Germany

³Applied Physics, Photonics & Semiconductor Nanophysics, Eindhoven University of Technology, 5600 MB, Eindhoven, The Netherlands

⁴NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, I-56127 Pisa, Italy

*email: alessio.campo@unibas.ch

Thermoelectric (TE) materials offer the possibility to convert the thermal energy lost during various power generation processes into electricity. Research in TE materials has been directed towards nanostructures that hold the promise of the realization of the high efficiency heat-electricity conversion [1]. The TE efficiency is usually quantified by the dimensionless figure of merit, $zT = \frac{\sigma S^2}{\kappa} T$, with σ electrical conductivity, κ thermal conductivity, S the Seebeck coefficient and T temperature. These parameters are strongly interdependent, making the optimization of zT extremely challenging [2][3].

Nanowires (NWs) are ideal candidates for exploring the effects of low dimensionality in TE applications, due to the theoretically predicted alteration of the density of states (thereby the increase of the power factor σS^2) and the enhancement of the phonon scattering (thereby a thermal conductivity suppression) [2]. Nevertheless, the development of a reliable technique that performs a complete assessment of the TE properties of nanostructures remains an experimental challenge. This is mainly due to the role of the thermal contact resistance between the NW and the platform used for the determination of the material properties [4-7].

We have determined the zT of InSb NWs using a novel method based on the hybridization of spatially resolved Raman spectroscopy and transport measurements [4]. We have provided experimental evidence of the crucial role played by thermal contact resistance in determining the thermal conductivity by comparing the above mentioned method with the well-established thermal bridge method [8].

1. Dresselhaus M S and Bell L E 2013 *Nat. Nanotechnol.* **8** 469
2. Hicks L D and Dresselhaus M S 1993 *Phys. Rev. B* **47** 16631–4
3. Kim W 2013 *Mater. Res. Innov.* **15** 375–85
4. Swinkels M Y *et al.* 2015 *Nanotechnology* **26** 385401
5. Yazji S *et al.* 2015 *Nano Res.* **8** 4048–60
6. Soudi A, Dawson R and Gu Y 2010 *ACS Nano* **5** 255–62
7. Liu D, Xie R, Yang N, Li B and Thong J 2014 *Nano Lett.* **14** 806–12
8. Yazji S *et al.* 2016 *Semicond. Sci. Technol.* **31** 064001

A Universal Method for Thermal Conductivity Measurements on Micro-/Nano-Films With and Without Substrates using Micro-Raman Spectroscopy

N. M. Wight^{1*}, E. Acosta¹, R. K. Vijayaraghavan², P. J. McNally², V. Smirnov³, and N. S. Bennett¹

¹Nano-Materials lab., Institute of Mechanical, Process & Energy Engineering, School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh. EH14 4AS, United Kingdom

²School of Electronic Engineering, Dublin City University, Glasnevin, Dublin 9. Ireland

³IEK-5 Photovoltaik, Forschungszentrum Jülich, 52425, Jülich, Germany

*email: nmw30@hw.ac.uk

The ability to measure intrinsic thermal conductivity via a non-contact, non-destructive process is extremely attractive. Micro-Raman spectroscopy has been demonstrated to enable effective non-contact thermometry with further work providing a non-destructive estimation of values for thermal conductivity on suitable materials. However significant limitations remain for nano- and micro-films. Materials that do not meet dimensional requirements for thickness or that are *in-situ* on a substrate or supporting structure present significant challenges using existing approaches. For such samples, representative measurements must be obtained using alternative methods that can compromise samples and/or require relative complexity in experimental design and analysis. Here an analytical model is shown allowing thermal conductivity to be measured free of such limitations via a straightforward approach using micro-Raman spectroscopy. Results are then obtained experimentally and values compared with those obtained using a complimentary technique demonstrating an improved accuracy over existing micro-Raman approaches. Furthermore, this model enables the effect of any substrate or supporting structure on measured values to be quantified and estimations for thermal conductivity of the sample itself to then be calculated where an influence is determined. Current estimations determining the threshold of substrate influence are shown to be insufficient and the importance of obtaining values of thermal conductivity for samples themselves under such conditions is demonstrated.

Optimization of Electrodeposited Bi₂Te₃-Based Thin Films for Realization of Thermoelectric Energy Harvester

Swatchith Lal, Devendraprakash Gautam and Kafil M. Razeeb

Micro-Nano Systems Centre, Tyndall National Institute, University College Cork,
Lee Maltings, Dyke Parade, Cork T12 R5CP, Ireland

Thermoelectric devices based on thin film technology are potential candidates for micro-thermoelectric generators/coolers (μ -TEG/ μ -TEC) for energy harvesting and cooling electronic devices. Bismuth telluride and its alloys have been extensively used as material for thermoelectric generators/coolers at near room temperature applications. The potential of a material for thermoelectric applications is evaluated by a dimensionless parameter called the figure of merit, zT and is defined as

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \quad (1)$$

where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature at which the properties are measured. For an efficient thermoelectric material zT should be as high as possible. Industrial up-scalability, cost-effectiveness and compatibility with Si-fabrication methods are the factors impeding the mass-scale production of the miniaturized thermoelectric devices. Electrodeposition of thin films is a facile, low cost process without the need for sophisticated high-vacuum equipment in contrast to other physical deposition methods, which is also Si-Fab compatible. Therefore, thermoelectric devices fabricated using electrodeposition can be directly fabricated and integrated at wafer scale for μ -TEG/ μ -TEC applications.

In the present work, we investigated comprehensively the influence of electrolytic bath content, deposition potential and surfactant on the composition and microstructure of thin films. Structural and chemical investigations of the as-deposited and annealed thin films are performed with X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. The impact of annealing temperature-time profile on the films microstructure and thermoelectric properties is thoroughly investigated. The annealed p - and n -type thin films exhibit a room temperature Seebeck coefficient of about 175 and -160 μVK^{-1} respectively. Thus, we synthesize the optimized electroplated bismuth telluride based alloy thin films with enhanced thermoelectric properties by tuning the composition and microstructure of the films through the deposition potential and annealing profile.

Thermal Conductivity of PbTe from Classical Molecular Dynamics Simulations

Javier Fernández Troncoso, Tchavdar Todorov, Myrta Gruening, and Jorge Kohanoff
Atomistic Simulation Centre, Queen's University Belfast, Belfast BT7 1NN, UK

Lead telluride (PbTe) is a reference high performance thermoelectric which can exhibit low values of thermal conductivity when it is doped. Although its crystal structure is stable, frozen phonon calculations show that the TO mode is very soft and its frequency near the Brillouin zone centre decreases with decreasing temperature. At the Γ point, this mode is directly related to the ferroelectric ground state and, as a ferroelectric material, it undergoes a phase transition to the cubic structure when increasing temperature (2nd order or weakly 1st order [1]) or pressure (1st order [2]).

In this work we analyzed the temperature dependence of the lattice thermal conductivity of PbTe. We studied a variety of models and classical force fields proposed in the literature, in particular a model based on the Buckingham potential [3] that gave very good results in comparison with experimental data. The lattice thermal conductivity was computed using two different methods – Green-Kubo and direct thermostating. Bo Qiu et al. [3] obtained their results via the Green-Kubo method with a simulation box consisting of 4x4x4 unit cells, which we considered insufficient. Using larger cells and finite-size extrapolation, we obtained converged values that are twice as large for the same potential. Our future goal is to improve on the interatomic potential to reproduce experimental data more closely, and hence focus on the region close to the phase transition in pure and doped PbTe, where important anharmonic effects arise [4].

1. T. Chattopadhyay, J. X. Boucherle, H. G. von Schnering, J. Phys. C: Solid State Phys. 20(10), 1431-1440 (1987)
2. Y. Fujii, K. Kitamura, A. Onodera, Solid State Comm. 49(2), 135-139 (1984)
3. B. Qiu, H. Bao, G. Zhang, Y. Wu, X. Ruan, Comput. Mater. Sci., 53, 278–285 (2012)
4. R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 93, 104304 (2016)

Finite-Temperature Properties of the Thermoelectric Clathrate Ba₈Al_xSi_{46-x}

Maria Troppenz, Santiago Rigamonti, and Claudia Draxl

Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany

Intermetallic clathrate compounds are promising candidates for high-efficiency thermoelectric applications. Here, we study Ba₈Al_xSi_{46-x} in the composition range $x \in [6,16]$ [1]. Recent theoretical studies [2] show a strong dependence of the electronic properties on configuration, i.e. the atomic arrangement of the substitutional Al atoms in the crystal framework. At the charge-balanced composition ($x=16$), the ground-state configuration is semiconducting. However, configurations higher in energy are metallic. Understanding this metal-semiconductor transition is essential, as semiconducting behavior is a prerequisite for thermoelectric applications. In this work, we employ the cluster expansion technique combined with Monte-Carlo simulations and the Wang-Landau method [3] to access finite-temperature properties, e.g. the temperature dependence of the band gap. We find that the transition is driven by a partial order-disorder transition of the substituents. Most importantly, it is found that the transition temperature (≈ 800 K) at the charge-balanced composition is close to the typical temperatures at which the figure of merit of thermoelectric clathrates is maximized. Signatures of the transition in the entropy, order parameter, specific heat, and canonical distribution are analyzed.

1. J. H. Roudebush et al.; Inorg. Chem. 51, 4161 (2012)
2. M. Troppenz, S. Rigamonti and C. Draxl; Chem. Mater. 29, 2411 (2017)
3. F. Wang and D. P. Landau, Phys. Rev. Lett. 86, 2050 (2001)

Thermal Expansion of $Pb_{1-x}Ge_xTe$ Alloys from First Principles

Djordje Dangić^{1,2}, Ronan Murphy^{1,2}, Éamonn Murray³, Stephen Fahy^{1,2}, and Ivana Savić¹

¹Tyndall National Institute, Cork, Ireland

²Department of Physics, University College Cork, Ireland

³Departments of Physics and Materials, Imperial College London, UK

Recently it was shown that driving PbTe near a structural phase transition by strain or alloying with GeTe could lead to a decrease in the thermal conductivity and possibly an increase in the thermoelectric efficiency of this material [1]. Using the theory of elasticity and Gruneisen theory within the quasiharmonic approximation of the vibrational properties of solids, we investigate the thermal expansivity of $Pb_{1-x}Ge_xTe$ alloys by minimizing the total Helmholtz free energy using density functional theory. We defined Gruneisen parameters with respect to structural degrees of freedom: lattice constant for rock-salt structure, and lattice constant, angle between primitive lattice vectors and the internal atomic displacement for rhombohedral structure, and used these to calculate thermal expansion coefficients.

We show that our approach reproduces experimental results for PbTe and GeTe reasonably well [2,3]. We find that accounting for the internal atomic displacement in the minimization of the total free energy for the rhombohedral phase of $Pb_{1-x}Ge_xTe$ alloys leads to discontinuities in their thermal expansion coefficients in the vicinity of the phase transition. There is large anisotropy of the thermal expansion coefficients in the rhombohedral phase with respect to the trigonal [111] axis. We also find that the thermal expansion coefficient in the direction parallel to the trigonal axis has negative thermal expansion. Our calculations show a considerable decrease in the volumetric thermal expansion coefficient in the rhombohedral phase near the phase transition, as observed experimentally in GeTe [2].

1. R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 95, 144302 (2017)
2. T. Chattopadhyay, J. X. Boucherle, and H. G. von Schnering, J. Phys. C 20, 1431 (1987)
3. R. Dalven, Infrared Phys. 9, 141 (1969)

Effect of Electron-Phonon Scattering on Thermoelectric Figure-of-Merit

Jiang Cao^{1*}, Ronan Murphy^{1,2}, Stephen Fahy^{1,2}, Ivana Savić¹

¹Tyndall National Institute, Dyke Parade, Cork, Ireland

²Department of Physics, University College Cork, Ireland

*email: jiang.cao@tyndall.ie

Thermoelectric power generators directly convert heat to electricity by using a temperature difference to induce charge carrier flow in a semiconductor. This solid-state, no moving-parts technology still has limited commercial use due to its low energy conversion efficiency. Great effort and progress have been made to increase thermoelectric figure-of-merit, ZT , defined as $ZT = S^2 \sigma T / (\kappa_e + \kappa_L)$ (S is Seebeck coefficient, σ is electric conductivity, and κ_e and κ_L are electronic and lattice thermal conductivity, respectively). A large part of work in the last decade focused on reducing the lattice part of the thermal conductivity by engineering phonon scattering mechanisms e.g. by nanostructuring. There is a limit to the improvement in ZT that can be achieved in this fashion, therefore leading us to investigate the possibilities to increase the power factor $S^2 \sigma$. In this work, we focus on the effect of elastic acoustic and inelastic polar optical phonon scattering mechanisms on ZT . The electronic band structure is described by a two-band Kane's model that accounts for non-parabolic effects when the electronic energy is far away from the band edge. Furthermore, semi-classical Boltzmann transport calculations are performed within the relaxation time approximation to determine the transport coefficients and ZT . Comparing with experimental results, we identify the importance of polar optical phonon scattering for PbTe, one of the most efficient thermoelectric materials. We establish the dependence of ZT on the form of the energy-dependent relaxation time determined by the scattering type. The results obtained will provide qualitative insights for improving ZT by engineering electron-phonon scattering.

Reducing the Thermal Conductivity by Driving PbTe to a Phase Transition via Strain and/or Alloying

Ronan Murphy^{1,2}, Éamonn Murray³, Stephen Fahy^{1,2}, and Ivana Savić¹

¹Tyndall National Institute, Cork, Ireland

²Department of Physics, University College Cork, Ireland

³Departments of Physics and Materials, Imperial College London, UK

Thermoelectric materials provide a means of generating electricity by harnessing waste heat. Lead telluride (PbTe) is a narrow gap semiconductor that crystallises in the rocksalt structure, and is known to be an effective thermoelectric material, particularly at high temperatures. The impressive figure of merit of PbTe is due to its characteristically low lattice thermal conductivity, which arises from its proximity to the ferroelectric phase transition. By driving PbTe to the verge of the phase transition to the rhombohedral structure, extremely soft optical modes are induced increasing acoustic-optical phonon coupling and decreasing phonon lifetimes at all frequencies. We demonstrate this concept by applying biaxial tensile (001) strain to PbTe and its alloy with rocksalt PbSe, and by alloying PbTe with a rhombohedral material, GeTe. We find that both alloying and tensile (001) strain efficiently scatter phonons across the entire frequency spectrum and significantly reduce the lattice thermal conductivity by a factor of ~2-3 in comparison to PbTe.

1. R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 93, 104304 (2016).
2. R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 95, 144302 (2017).

Day 3

Wednesday July 5th, 2017

Session 1

Tellurides

8:30-10:10

Substitutional Behaviour of Lead Telluride

Xinke Wang¹, Igor Veremchuk¹, Jing-Tai Zhao², and Yuri Grin¹

¹ Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

² Shanghai University, Shanghai, China

With low thermal conductivity and excellent electronic transport properties, the semiconductor lead telluride is one of leading thermoelectric materials in mid-temperature range. To enhance the thermoelectric performance of PbTe, optimizing the carrier concentration and band structure engineering are usually carried out by chemical substitutions. The reasons for this modification lie in the physical-chemical behavior of the binary phase: the temperature-dependent studies of the binary phase reveal that its homogeneity range changes with temperature.

In contrary the literature data, the extension of the solid solution $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ only for $0 \leq x \leq 0.02$ was found. No supposed strong influence of the lead-by-europium substitution on the thermoelectric figure-of-merit was observed in the stoichiometric bulk materials. Further substitution by sodium enhances the ZT value of the bulk material above 2.0. Substitution of Te by antimony allows to reach the ZT values larger as one above 500 °C.

Crystallography of Thermoelectric Tellurides

Oliver Oeckler

Institute of Mineralogy, Crystallography and Materials Science; Faculty of Chemistry and Mineralogy, Leipzig University, Scharnhorststr. 20, 04725 Leipzig, Germany
email: oliver.oeckler@gmx.de

Some fundamental limitations concerning the thermoelectric performance of compounds with ideal, completely ordered crystal structures may be overcome by new concepts that involve severely disordered, nanostructured and/or heterogeneous materials. Nanostructured tellurides represent some of the most efficient material systems. Domain structures in chemically homogeneous systems may result from “incomplete” diffusion-controlled phase transitions, structural vacancies playing a crucial role. As exemplified by germanium antimony tellurides (GST materials) and related compounds,^[1] temperature-dependent structural changes involve complex ordering mechanisms but may still afford materials that are long-term stable. Approaches towards controlling defect concentration and distribution include a plethora of chemical substitutions. These influence phase-transition temperatures and thus the nanostructures formed but also electronic properties.

Such disorder involves diffuse X-ray scattering which can be quantified using novel methods such as the 3D- Δ PDF^[2] in combination with TEM imaging. Resonant X-ray scattering is an ideal method to determine the element distribution in multinary systems that contain several elements with similar electron counts. Synchrotron radiation further enables the *in situ* observation of structural changes upon thermal treatment.^[3] This is also essential for the analysis of dynamical disorder, i.e. highly mobile atoms in PLEC (phonon-liquid electron-crystal) materials. Li atom mobility is also being investigated by solid-state NMR spectroscopy and quasi-elastic neutron scattering.

Moreover, research increasingly focuses on chemically inhomogeneous systems. Ideally, these contain nanoscale precipitates endotaxially intergrown in a matrix that itself exhibits disorder and a domain structure. Skutterudite-type or cobalt germanide precipitates in GST materials demonstrate how nano- and microcrystallites significantly enhance the thermoelectric properties.^[4] In more complicated systems such as Cu-doped GST, mutual doping of matrix and precipitates needs to be considered. A new approach that exploits the advantages of both transmission electron microscopy and microfocused synchrotron radiation even enables the precise structure determination of single sub-micron sized crystallites.^[5]

1. T. Rosenthal, P. Urban, K. Nimmrich, L. Schenk, J. de Boor, C. Stiewe, O. Oeckler, Chem. Mater. 26 (2014) 2567; S. Welzmler, F. Fahrnbauer, F. Hennersdorf, S. Dittmann, M. Liebau, C. Fraunhofer, W. G. Zeier, G. J. Snyder, O. Oeckler, Adv. Electron. Mater. 1 (2015) 1500266; T. Rosenthal, L. Neudert, P. Ganter, J. de Boor, C. Stiewe, O. Oeckler, J. Solid State Chem. 215 (2014) 231.
2. P. Urban, A. Simonov, T. Weber, O. Oeckler, J. Appl. Crystallogr. 48 (2015) 200.
3. M. N. Schneider, X. Biquard, C. Stiewe, T. Schröder, P. Urban, O. Oeckler, Chem. Commun. 48 (2012) 2192; P. Urban, M. N. Schneider, O. Oeckler, J. Solid State Chem. 227 (2015) 223.
4. F. Fahrnbauer, S. Maier, M. Grundei, N. Giesbrecht, M. Nentwig, T. Rosenthal, G. Wagner, G. J. Snyder, O. Oeckler, J. Mater. Chem. C. 3 (2015) 10525; F. Fahrnbauer, D. Souchay, G. Wagner, O. Oeckler, J. Am. Chem. Soc. 137 (2015) 12633.
5. F. Fahrnbauer, T. Rosenthal, T. Schmutzler, G. Wagner, G. B. M. Vaughan, J. P. Wright, O. Oeckler, Angew. Chem. Int. Ed. Engl. 54 (2015) 10020.

Supercell Modeling of Na and Tl Doping of Lead Telluride

Pavel Korotaev, Andrey Mukhanov, Alexey Yanilkin

Center for Fundamental and Applied Research, Dukhov Research Institute for Automatics,
Moscow, Russia

Transport properties of PbTe were studied in semi-classical approach with electronic structure obtained by first-principles calculations. Supercell model of doping was used, i.e. supercells of $\text{MePb}_{31}\text{Te}_{32}$ and $\text{MePb}_{47}\text{Te}_{48}$ where Me = Na or Tl (3.12 and 1.56 at. %). Spin-orbit coupling was taken into account.

It was shown that supercell model of doping leads to lowering of Seebeck coefficient values, in comparison with conventional rigid band approximation in both cases of Na and Tl doping. In the case of Tl doping the density of Tl states near valence band edge is much higher, than is the case of Na. However, direct calculated Seebeck coefficient of Tl-doped PbTe is not higher, than in the Na-doped. Therefore, the known increase in Seebeck coefficient in $\text{Tl}_{0.02}\text{PbTe}$ may be related not only to the distortion in the electronic density of states.

Day 3

Wednesday July 5th, 2017

Session 2

2D and Layered Materials

10:20-12:00

First Principles Modelling of Thermo-electrics Using ATK, Comparison of Bulk and Full Device Approaches

Troels Markussen

QuantumWise A/S, Fruebjergvej 3, 2100 Copenhagen, Denmark

troels.markussen@quantumwise.com

The Atomistix ToolKit [1] contains a broad range of functionalities for first principles modelling of electrical and thermal transport in nano-scale systems. For ideal bulk system it is possible to model electrons, phonons and electron phonon interactions, and via the Boltzmann equation obtain relevant transport coefficients for thermo-electric systems [2]. For nanoscale devices it is possible to calculate coherent electron and thermal transport coefficients using NEGF. Recently we have developed simple finite displacements methods which allows in a simple way to include the effect of electron-phonon coupling in the calculation of the transports coefficients [3].

In this presentation, I will briefly describe the theoretical background of the methods and their application range. I will compare the different methodologies for calculating the electrical and thermal transport coefficient and thermo-electric figure of merit for a number of test systems.

1. www.quantumwise.com/products
2. T. Gunst, T. Markussen, K. Stokbro, and M. Brandbyge. *First-principles method for electron-phonon coupling and electron mobility: Applications to two-dimensional materials*. Phys. Rev. B, **93**(3), 035414 (2016).
3. T. Markussen, M. Palsgaard, D. Stradi, T. Gunst, M. Brandbyge, and K. Stokbro. *Electron-phonon scattering from Green's function transport combined with Molecular Dynamics: Applications to mobility predictions*. arXiv preprint arXiv:1701.02883 (2017).

About QuantumWise

QuantumWise develops software for simulating electrical and materials properties at the atomic-scale. The software is used by the major semiconductor companies, in the chemical and materials industry, as well as several hundred universities and government labs. The company builds on the long tradition for quantum mechanical research in Denmark and employs a team of top European PhDs in physics, chemistry and computer science. The Company was started in 2008 and has +30 employees worldwide. The company is headquartered in Copenhagen, Denmark with subsidiaries in Japan and USA and local representation in Singapore. It is privately owned and has recent years shown 30% organic growth rates. It is a 2015 and 2016 Børsen Gazelle company.

Full Thermoelectric Characterisation of Hot Pressed Solution Processed Group VI TMD Films around Room Temperature

Graeme Cunningham^{1*}, Ryan Enright¹, David McCloskey², Emmet Byrne², and Jonathan Coleman²

¹Bell Labs Ireland, Blanchardstown Business & Tech Park, Snugborough Rd, D15 Y6NT, Ireland

²CRANN, the Naughton Institute, Trinity College Dublin, Pearse St, Dublin 2, Ireland

*email: grcunnin@tcd.ie

In this work we perform a thermoelectric (TE) material survey of the full family of group VI TMDs (MoS₂-WTe₂) produced by solution processing methods. Full ZT characterisation (σ , S and κ) has been carried out in the temperature range around room temperature. Whilst recent theoretical studies show such materials may make for promising TE materials, no experimental TE studies exists for this set of materials produced by such an approach previously. In addition to its many well-known existing benefits, solution processing can be particularly beneficial for producing films of TE material as they inherently contain a high interface density; which serves to attenuate the lattice component of the thermal conductivity.

Here we have applied size selection methods of the commercial TMD powders dispersed in NMP to remove the smallest flakes which are known to be more prone to oxidation in atmosphere. Films of 100 μm thickness have been formed by vacuum filtration onto PTFE membranes which are then cut into 1 cm^2 pieces before being hot pressed at a pressure of 65 kN at 150 °C for 10 minutes, in order to densify the porous networks normally characteristic of solution processed films. This has the added benefit of boosting the obtainable electrical conductivity by a full two orders of magnitude in all cases, concomitantly enhancing the power factor.

This work highlights the most promising of this family of solution processed layered materials for thermoelectric applications in their bulk form, in addition to informing which ones may be most suitably combined to make higher ZT nanocomposites in the future.

Insight into Thermoelectric Properties of High-Performance Layered Oxides: A Cooperative Computational and Experimental Study

J.D. Baran¹, D.M. Kepaptsoglou², F. Azough³, M. Molinari⁴, S.C. Parker¹, Q.M. Ramasse², and R. Freer³

¹Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

²SuperSTEM Laboratory, SciTech Daresbury Campus, Daresbury WA4 4AD, UK

³School of Materials, University of Manchester, Manchester, M13 9PL, UK

⁴Department of Chemistry, University of Huddersfield, Huddersfield, HD1 3DH, UK

Misfit layered cobalt oxides $(M_2CoO_3)_{0.6}CoO_2$ ($M = Mg, Ca, Sr, Ba$)[1] and $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ (BSCO)[2] exhibit remarkable physical properties and show great promise as high temperature thermoelectric materials. They are composed of two incommensurate subsystems – crystalline CoO_2 layers and rocksalt-type (RS) $Ca_2Co_3/BiSrO_2$ layers. In our work, we apply density functional theory, Boltzmann transport equation and high-resolution transmission electron microscopy to investigate the relationship between structural, electronic, vibrational and thermoelectric transport properties in this class of materials. We identify the most stable structures and present structural models that agree well with both bulk and atomic-scale experimental data. In addition, we provide data on their electronic, magnetic and transport properties. We investigate the relationship between the hole-doping mechanism and the Bi defect, through the changes of the local structure and show that Bi-deficiency leads to a band-gap opening and increases p-type electronic conductivity of the material due to formation of Co^{4+} species that serve as itinerant holes within the predominantly Co^{3+} framework of CoO_2 layer. The reliability of the simulations is supported by the calculated temperature dependence of the Seebeck coefficient for the Bi-deficient system, which is in good agreement with the measurements further stressing the importance of the Bi deficiency for this material. Moreover, we shed light on the apparent stacking disorder of the RS layers that can take different arrangements between CoO_2 layers. We find that such a disorder arises from the minor energetic difference between different relative arrangements of CoO_2 and RS layers in consecutive layers of BSCO and can be related to the low thermal conductivity of the material. Our study shows that the first principle calculations can provide detailed understanding of the properties of these complex materials, which make them a valuable tool for developing and testing new oxide thermoelectric materials.

1. Baran J. D. et al., *Tuning Thermoelectric Properties of Misfit Layered Cobaltites by Chemically Induced Strain*, Journal of Physical Chemistry C, 2015, **119**(38): p21818-21827
2. Baran, J.D., et al., *Role of Structure and Defect Chemistry in High-Performance Thermoelectric Bismuth Strontium Cobalt Oxides*. Chemistry of Materials, 2016.

Day 3

Wednesday July 5th, 2017

Session 3

Half-Heuslers

13:30-15:30

Thermoelectric Materials for the Medium- and High-Temperature Range (600 K < T < 1200 K)

***A. Weidenkaff, W. Xie, X. X. Xiao, and T. Zou**

Institute for Materials Science, University of Stuttgart, Heisenbergstr. 3, DE-70569 Stuttgart,
Germany

*weidenkaff@imw.uni-stuttgart.de

Thermoelectric materials for different operating temperatures ranges, such as manganese tellurides ($T < 700$ K), half-Heusler compounds ($T < 1000$ K), and perovskite-type oxides ($T > 1000$ K), have been developed and tested. In order to obtain high efficiency thermoelectric materials and devices, the relation between sample preparation methods, microstructures, and transport properties are deeply investigated. Perovskite-type ceramics, stable Heusler compounds and chalcogenides as well as their nanocomposites are prospective candidates for high temperature thermoelectric energy conversion processes [1-3]. Their good performance can be explained based on e.g. their suitable band structures, adjusted charge carrier density, effective mass and mobility, hindered phonon transport, electron filtering potentials, and strongly correlated electronic systems. These properties are tuneable by changing the composition, structure, crystallites size, interfaces and materials combinations with tailor-made scalable synthesis procedures. The design of the experiments is based on theoretical predictions and a deep knowledge on composition-structure-property relationships. The resulting improved thermoelectric materials are characterised and tested in diverse high temperature applications to improve the efficiency and energy density of the thermoelectric conversion process. The goal of our research is to finally utilize the investigated materials to convert large temperature gradients of waste heat into electricity.

Thermoelectricity by Rational Design: New Materials and Insights from First-Principles Computations of Carrier Scattering

Georgy Samsonidze

Research and Technology Center, Robert Bosch LLC, Cambridge, MA, USA

Accelerated discovery of next-generation materials for thermoelectric energy conversion requires capability for efficient prediction of materials' performance from first-principles, without empirically fitted parameters. We introduce a novel simplified approach for computing electronic transport properties, which achieves good accuracy and transferability while greatly reducing complexity and computation cost compared to the existing methods. Our first-principles calculations of the electron-phonon coupling tensor demonstrate that the energy dependence of the electron relaxation time varies significantly with chemical composition and carrier concentration, suggesting that it is necessary to go beyond the commonly used approximations to screen and optimize materials' composition, carrier concentration and microstructure. We verify the new method using high accuracy computations and validate with experimental data before applying it to screen and discover promising compositions in the space of half-Heusler alloys, technologically relevant for waste heat recovery. Using the new tool we discuss the universality of the Wiedemann-Franz law and identify the effective electron mass as the single best general descriptor determining material's performance.

Unveiling the Role of Defects in Thermal Transport: an Ab Initio Study Using AlmaBTE Code

Ankita Katre

LITEN, CEA-Grenoble, France

Defects are ubiquitous in materials and can have large effects on their thermal conductivities. However, it has been a challenge to date to theoretically predict these effects. Using our ab initio approach based on Green's function formalism [1] implemented in almaBTE software (www.almabte.edu), we find excellent agreement of thermal conductivities for various technologically relevant defective materials with experiments [2,3]. Furthermore, unique behaviours of defects are also revealed in our studies, which are not captured by commonly used simple modeling approaches. For example, our study on thermoelectric half-Heusler compound ZrNiSn unveils that Ni/vacancy antisites, and not the previously claimed Sn/Zr antisites, are the dominant defects affecting its thermal transport [2]. Additionally, we find a sixth power dependence of phonon-antisite scattering rates on the phonon frequency, which is different from the usually considered fourth power dependence. Another study on cubic SiC shows an exceptionally strong effect of BC on its thermal conductivity as compared to other defects as NC and AlSi [3]. We find that such striking behaviour of BC defect arises from a unique pattern of 'resonant phonon scattering' caused by the broken structural symmetry around the boron impurity atom. Thus our approach captures the actual behaviours of defects in a material leading to good agreement of calculated thermal conductivities with experiments. In my talk, I will elaborate on these interesting findings for ZrNiSn and SiC and their implications on materials designing and characterization, along with an introduction to our novel ab initio approach.

1. N. Katcho et al., Physical Review B , 90, 094117 (2014).
2. A. Katre et al., under review in Physical Review Letters, arXiv:1703.04996 (2017).
3. A. Katre et al., Journal of Materials Chemistry A, 4, 15940 (2016).

Day 3

Wednesday July 5th, 2017

Session 4

Thermoelectric Transport Modelling

16:00-18:00

Nonequilibrium Thermal Density Functional Theory - a Microscopic Approach to Thermoelectric Transport

Giovanni Vignale

Department of Physics, University of Missouri, USA

We review nonequilibrium Thermal Density Functional Theory, a novel approach to address charge and energy transport from first principles. The description of the interplay between charge and energy degrees of freedom is essential for the prediction of thermoelectric transport coefficients based on the microscopic Hamiltonian. The idea behind Thermal DFT is therefore to include the energy density as a basic variable. We discuss how the requirement of reproducing the interacting energy density using a system of fictitious non-interacting Kohn-Sham electrons leads to the appearance of a novel coupling term in the Hamiltonian. This new coupling term had already been introduced by Luttinger several decades ago to compute the thermal conductivity by using the Kubo's linear response formalism. We argue that the new coupling term can be interpreted as a mechanical analogue for local temperature variations and, hence, opens a route to define local temperature at the nano scale.

Thermoelectric Properties from First-Principles via the Exact Solution of the Boltzmann Transport Equation

Nicola Bonini

Department of Physics, King's College London, London, UK

A detailed understanding of electrical transport phenomena is crucial for the discovery and the development of high-performance materials for thermoelectric energy conversion technologies. In this talk, we present a first-principles computational approach to calculate thermoelectric transport coefficients via the exact solution of the linearised Boltzmann transport equation, also including the effect of non-equilibrium phonon populations induced by a temperature gradient. We use density functional theory and density functional perturbation theory for an accurate description of the electronic and vibrational properties of a system, including electron-phonon interactions; carriers' scattering rates are computed using standard perturbation theory, exploiting Wannier interpolation for an efficient sampling of the Brillouin zone. We discuss the application of this approach to sp-bonded semiconductors, focusing on electrical conductivity, Lorenz number and Seebeck coefficient, including the phonon drag effect, in a range of temperatures and carrier concentrations. This approach gives results in good agreement with experimental data and provides a detailed characterization of the nature and the relative importance of the individual scattering mechanisms. Moreover, the access to the exact solution of the Boltzmann equation for realistic systems provides a direct way to assess the accuracy of different flavors of relaxation time approximation, as well as of models that are popular in the thermoelectric community to estimate transport coefficients.

Study of the Effect of the Scattering rate on the Thermopower

Philip Murphy-Armando

Tyndall National Institute, Dyke Parade, Cork, Ireland

I will explore the effects of different types of scattering on the thermopower S of SiGe alloys at various temperatures and doping concentrations. Usually, the effect of the scattering rates on S is assumed to be negligible, especially if the relaxation times are taken as energy-independent [1]. This is often the case, but as we shall see, there are many instances in which a reduction in scattering, resulting in an increase of conductivity, also favourably affects the Seebeck coefficient. This effect chiefly depends on the energy profile of the scattering in question [2]. Of course there is a shape of the energy dependence of the scattering kernel that optimises ZT , found by Mahan and Sofo [3]. In essence, it is a delta function in energy. Many efforts have gone into achieving this optimum shape, for example by the use of impurity energy states [4.] I have calculated various scattering mechanisms already present in doped SiGe alloys from first principles [5-7], which differ in their energy dependence. By varying their relative strength, we can gain some insight into the effects of the energy profiles in a natural way.

1. G. K.H. Madsen and D. J. Singh, *Computer Physics Communications*, 175, 67 (2006).
2. B. Xu and M. J. Verstraete, *Phys. Rev. Lett.*, 112, 196603 (2014).
3. G.D. Mahan and J.O. Sofo, *PNAS*, 93, 7436 (1996).
4. J. P. Heremans et al., *Science*, 321, 554 (2008).
5. F. Murphy-Armando and S. Fahy, *Phys. Rev. Lett.*, 97, 096606 (2006).
6. F. Murphy-Armando and S. Fahy, *Phys. Rev. B*, 78, 035202 (2008).
7. F. Murphy-Armando and S. Fahy, *J. Appl. Phys.*, 110, 123706 (2011).

About the Electronic Properties of Fe₂VAI and Related Thermoelectric Compounds

Fabio Ricci, Sébastien Lemal, Matthieu J. Verstraete and Philippe Ghosez
Theoretical Materials Physics, Q-MAT, CESAM, University of Liège, Belgium

Fe₂YZ full-Heusler compounds recently appeared as promising candidates for thermoelectric applications. Based on first-principles density functional theory (DFT) calculations, they were indeed predicted to exhibit very large thermoelectric power factor [1]. Of course, the quality of this type of theoretical prediction relies on the ability to correctly access the electronic properties, which may require going beyond the most usual approximations. Although not predicted to be the most efficient, Fe₂VAI is the most studied compound of the Fe₂YZ family. Experimentally, it is controversially described either as a semi-metal or a semiconductor. Theoretically, standard DFT calculations predict the system to be a semi-metal with a narrow pseudo-gap but cannot be fully conclusive on the real nature of the system [2]. More recently, hybrid functional simulations (DFT-HF) clarified the nature of Fe₂VAI: they suggested that the pure compound is a narrow gap semiconductor while the semi-metallic character can be induced by the presence of lattice defects or atomic disorder [3]. Besides that, methods beyond the standard DFT, exploiting for example the on-site Hubbard-U Coulomb repulsion (DFT+U) suggest that 3d electrons belonging to Fe and V atoms experience strong correlations [4]. Here, we will show that self-consistently-optimized U parameters converge to robust values, which however provide a rather different description of the electronic structure than the hybrid functional approach. We will contrast DFT+U and DFT-HF results, comparing them with experiments and discussing consequences on the description of the thermoelectric properties of Fe₂VAI and other related Fe₂YZ compounds.

1. D. I. Bilc et al., Phys. Rev. Lett. 114, 136601 (2015).
2. D. J. Singh and I. I. Mazin, Phys. Rev. B 57, 14352 (1998).
3. D. I. Bilc and Ph. Ghosez, Phys. Rev. B 83, 205204 (2011).
4. D. Do et al., Phys. Rev. B 84, 125104 (2001).