Report on workshop « Thermoelectric Transport: progress in first principles and other approaches and interplay with experiment »

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Overview :
This 3 day workshop has gathered 48 researchers from 12 different countries in Europe, Asia, and North America. One main goal was to review the state of the art in theoretical computations of thermoelectric transport, and the interaction between theory and experiment.

The workshop was structured into three major topics: novel materials for thermoelectrics (day 1), thermal transport (day 2), and materials by design (day 3). In addition to the oral talks, the workshop featured a poster session, and a public panel discussion on the issue of “overcoming the ZT barrier.”

About 1/4 of the participants were students or postdocs. Financial support was provided by Cecam, the European Science Foundation-Intelbiomat, Psi-k, Ecole Polytechnique, ONR-Global, and three different departments from the French Atomic Energy Commission: LITEN (Grenoble), CEA-DSM, and CEA-DSM-Iramis.

Highlights from each session

Day 1: Novel materials for thermoelectrics

Opening remarks were delivered by **N. Vast**.

The morning sessions addressed novel “powder and nanoparticle composites.” **Gang Chen from MIT, Boston** discussed new Bi2Te3 and SiGe composites produced by the ball milling and sintering approach, where important increases in ZT have been recently reported due to a reduction in thermal conductivity. He then discussed the theoretical estimation of phonon mean free paths, and illustrated it in the case of Si and nanoporous Si. He underlined that there does not seem to be a clearly unified view of the “scattering” and “group velocity modification” effects on phonon transport. Afterwards**, A. Shakouri from UCSC, Santa Cruz** made an emphasis on thermoelectric properties of thin-film superlattices. He showed experimental and modeling results on several systems, in particular new metal-semiconductor superlattices based on (Zr,W)N/ScN for high temperature applications. He also discussed the fact that ZT looses its meaning when dealing with inhomogeneous materials, and one can increase the maximum cooling of a thermoelectric refrigerator beyond the theoretical value given by ZT, using a graded structure. Student **M. Zebarjadi from UCSC** (who received a fellowship from UIUC to attend the workshop) discussed the features of scattering potentials needed to increase the power factor. Then she elucidated recent experimental results that she successfully compared with theory. Some empirical results regarding the dependence of carrier concentration are still not understood.

The last session of the morning and the afternoon sessions were devoted to new bulk materials. Skutterudites were discussed in a very interesting presentation by **W. Zhang from SICCAS, Shangai**. He focused on the filling fraction limits for CoSb3, and showed theoretical predictions and their experimental confirmation, allowing to increase the ZT. The promising potential of new boron based materials was addressed by **T. Mori from NIMS, Tsukuba**, in a very clear presentation. Based on his experimental results he identified disorder as a main source of thermal conductivity reduction, discarding several alternative possibilities. Borides were further theoretically discussed by **E. Betranhandy from E. Polytechnique, Palaiseau, France** who elucidated the reasons behind some of the unusual mechanical properties of boron carbide. **J. Heremans from Ohio State** gave a highly illuminating presentation on two very new topics: increasing the Seebeck coefficient via resonant states, and decreasing the thermal conductivity by creating highly anharmonic phonon modes. He gave an exemplary account of the interaction between experiment and theoretical modeling. As an experimentalist, he further posed a list of requests to theorists, in particular the need for accurate phase diagrams, temperature dependent band structures, and more simple models that can be used to predict trends without the need of complicated numerical simulations. Closing the session, the interesting area of oxide thermoelectrics (Cobaltates) was discussed by **M. Roger from CEA, Saclay**. He provided a nice example of how complex condensed matter theory plays a role in understanding the structural and electronic properties of these particular systems.

Day 1 Poster Session
The afternoon poster session covered a range of subjects including the role of disorder on thermal transport in graphene nanoribbons, InP nanowires, and nanoporous materials, thermoelectric properties of $MgSi_2$ and Bi_2Te_3 from first principles, electron-phonon interactions, and effects of surface roughness on transport properties. These topics led to some lively discussions.

Photos from the poster session on Day 1. Starting from the top left and going clockwise, [1] J. Heremans, Anna Drozdova, and Elena Rogacheva, [2] Paul von Allmen, Jelena Sjakste [3] Nathalie Vast, Chandan Bera[4] Pawel Keblinski and Haldun Sevincli discuss thermal transport in graphene.

Day 2: Thermal transport

The second day was fully devoted to thermal transport. Morning talks focused on bulk and composite materials**. S. Volz from Ecole Centrale, CNRS, Châtenay-Malabry** presented Monte Carlo simulations of thermal transport in nanoporous alloys, showing an interesting potential for thermal conductivity reduction. An experimental account of thermal conductivity measurements on quantum dot Si/SiGe multilayers was provided by **F. Pezzoli, IFW Dresden**. He showed new results with rather low thermal conductivities. **I. Savic from CEA, Grenoble** presented Green's function atomistic calculations of thermal conductivity in disordered and nanostructured SiGe. The problem of predictive ab-initio calculation of the thermal conductivity of periodic crystals was presented by **D. Broido from Boston College**. He showed state of the art ab-initio calculations of the thermal conductivity of bulk Si, Ge, and C, in excellent agreement with experimental measurements. **P. Keblinski from RPI** presented a molecular dynamics study of WSe_2 layered structures which have highly anhisotropic thermal transport like graphite but also have ultralow thermal conductivity below the amorphous limit. He also discussed how random networks of high thermal conductivity nanotubes dramatically reduce the composite thermal conductivity.

In the afternoon, talks focused on thermal transport across interfaces. **G. Mahan, from Pennsylvania State University,** presented possibly the first theoretical calculation of metal-dielectric interface thermal conductance that agrees with experimental measurements. Afterwards, **K. Esfarjani from UCSC** showed ab-initio Green's function calculations of thermal conductance in graphene junctions, and discussed the impossibility of observing quantization when the junctions are abrupt. **D. Stewart from Cornell** presented an ab-initio

Green's function approach to isotope disordered BN nanotube thermal transport, which explains previous experimental results.

PANEL DISCUSSION ("Beating the ZT Barrier: Issues and Future Directions")

A panel discussion followed, where some key issues on the present and future of thermoelectrics research were discussed. The panel was composed by Gang Chen, Giulia Galli, Pawel Keblinski, Joseph Heremans, Gerry Mahan, Ali Shakouri, Derek Stewart, and Paul Von Allmen. J-P Issi posed the following questions to the panel:

o What are the urgent challenges to our theoretical understanding of bulk materials? Can we say we theoretically understand such a commonplace material as bulk Bi_2Te_3?

o Directions in nanocomposites. How far can we push the limits of phonon-blocking without electron blocking?

o Band structure engineering for power factor enhancement. Success has come via resonant states, but not yet via the original superlattice quantum confinement proposed in the 90's. Are we still very far from the Hicks-Dresselhaus paradigm?

o The ZT barrier. Does the long term future reside in overcoming this barrier with increasingly better materials? Or rather in going around it, by some radically new concepts beyond the traditional thermoelectric circuit?.

o Career advice to participating students and postdocs. Where should they focus their efforts?

Some main views and conclusions on these topics were:

On the experiment-theory interplay:
We understand power factor better than we understand thermal conductivity (G. Mahan). An important advancement on the latter was shown by D. Broido in the morning (G. Mahan). We need reproducibility and repeatability of experiments. This is more and more of a problem nowadays with nanoscale measurements. Even in pure materials like Si nanowires, we have not established yet the knowledge about technical issues nor about approximations, despites the fact that we compare theoretical results (G. Galli). Some kind of standardization, for theory as well as for experiment, is needed. Including input files used in simulations as part of the supplementary material for peer reviewed papers was mentioned as one route to provide checks and better confidence of results (D. Stewart).

On Hicks and Dresselhaus' original idea:

There is no fundamental reason why the Hicks-Dresselhaus concept would not work. In practice, it does not apply because of parasitic effects. Singularities in the density of state disappear as soon as you have a slight inhomogeneity (Shakouri). There are no large-scale confined materials for thermoelectricity : one needs a filling factor of more than 50%. One suggestion was to impregnate nanopores with Bi2Te3 (Heremans).

On the relevance of enhancing ZT:
Efficiency (ZT) is not the only issue. Another factor is cost (Shakouri).
Interfaces are an issue on top of ZT. Even a good ZT can be undermined by high interface resistance. One theoretical problem is to describe solid/solid interface (Keblinski).
Thermoelectric power generation is still very desirable in applications below 1 KW, because mechanical systems are less efficient at low power levels. The main interest is mobile applications (Issi). (And nobody had ever claimed on the contrary.) If you want to describe a thermoelectric device, ZT is OK if the material is uniform, but if macroscopically, the material is inhomogeneous, then one should average the conductivity, etc, and the average ZT is wrong (Galli and Shakouri). The market for cooling materials is larger. ZT doe not apply to compare efficiency of thermoelectrics cooler with respect to mechanical refrigerator, because the latter involves a phase transition (Shakouri) An increase of ZT by 10% would double the business of a small company as long as you can make it cheaper (Mahan). Heat is wasted by the buildings. It could be reconverted by thermoelectricity (Galli). The cost of a solar cell is around 3$/W. And for a solar cell and the installation, it amounts to 7$/W/. The cost for a thermoelectrics is 7$/W. But materials is not the only point. Devices for input heat and output heat is also very important and must be reduced (Chen). In China, the cost of the energy is not the same. Energy is basically costless, so that ZT~1 is not enough (audience, Zhang).

Heremans, on new materials and Te-free compounds:
There has to be room to new ideas, and for Te-free materials, because Te is not available, and actual cost is anomalously low. But we also need to get the field to expand, and in order to do so, we need to put something on the market rapidly. For this, we need to find shortcuts. The dominant cost is in contacts. We have the contact technology for PbTe, and not for iron silicide, for instance. Only then can we show society the interest of thermoelectrics, and ensure the expansion of the field. That is why he works on PbTe and Bi_2Te_3.

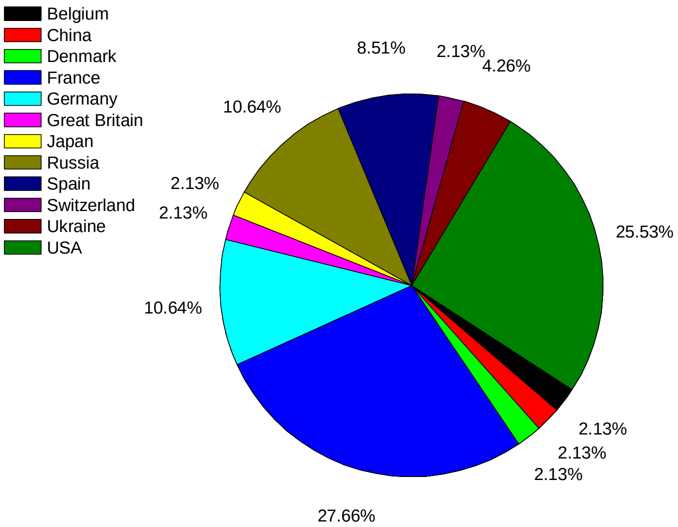
On education and thermoelectrics:
Chen: Thermoelectrics is a beautiful problem. It is fully multidisciplinary: you have to treat heat, electronics and materials. There are many options. You can learn a lot of fundamentals, and you can go create a startup. Energy becomes as important as biotechnology (Keblinski).
Heremans: there is no general advice. Each student is different, and it is the advisor's responsibility to orient the student in the most suitable way.

Day 3: Materials by Design

The morning session included several approaches involving rather heavy numerical simulation. **G. Cuniberti, TU Dresden** discussed the effects of Anderson type disorder to lattice thermal conductivity of carbon nanotubes using an atomistic Green function approach. He showed that ballistic, diffusive and localization transport regimes for phonons of different energies coexist and their relative weight on the thermal conductance depends on temperature. An interesting method for crystal structure prediction using a novel evolutionary algorithm was presented by **A. Lyakhov, Stony Brook, New York**. An example of this approach demonstrated that transparent insulating states of sodium occur under pressure. **Giulia Galli , University of Davis, California**, discussed her group's development of quantum mechanical simulation tools to understand and predict properties in nanostructured materials at the microscopic scale. She described molecular dynamics, lattice dynamics, and Boltzmann transport equation calculations to understand heat transport in Silicon nanowires. Then **P. Von Allmen, Pasadena, California** discussed his group's approach to computing thermoelectric properties of nanostructured materials using parameterized tight-binding models demonstating good agreement with experiment for Bi_2Te_3. First principles results for the electron-phonon coupling and electrical conductivity and electronic component of the thermal conductivity for Mg_2Si were presented by **P. Boulet, University of Aix-Marseille**.

The afternoon was devoted to discuss new approaches to electron transport, and electron phonon interactions. **P. Kratzer, University Duisburg-Essen**, discussed his model for thermoelectric properties of 1D stacks of InAs/GaAs quantum dots. He implemented a full solution of the Boltzmann equation for electonic transport to calculate the thermoelectric power factor and showed a small range of parameter space in which it could be enhanced. The issues of electron filtering and nanoparticle composites were revisited by **Shidong Wang**, CEA, Grenoble, who introduced Green's function calculations applied to the effect of interface roughness in nanostructures. Finally, **J. Sjakste, Ecole Polytechnique, Palaiseau** gave an account of novel ab-initio computations of electron-phonon interactions in bulk semiconductors and short-period superlattices.

Closing remarks were delivered by **D. A. Broido**.



Distribution of Participants by Country

List of Participants

Belgium

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China

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Min Chen (Institute of Energy Technology, Aalborg University, Denmark)

France

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Pascal Boulet (Laboratory of Chemistry, Aix-Marseille I University, France)
Laurent Chaput (Laboratoire de Physique et de Spectroscopie Electronique, Universite de Haute-Alsace)
Marie-Christine Record (Aux-Marseille University)
Michel Roger (CEA-Saclay)
Ivana Savic (CEA Grenoble)
Jelena Sjakste (CNRS, Ecole Polytechnique, Palaiseau)
Konstantinos Termentzidis (CETHIL, INSA de Lyon)
Sebastian Volz (Ecole Centrale de Paris)
Shidong Wang (CEA Grenoble)
Natalio Mingo (CEA Grenoble)
Nathalie Vast (Laboratoire des Solides Irradiés, Ecole Polytechnique)

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