HL 24: Thermoelectricity

Time: Tuesday 9:30–13:00 Location: EW 202

HL 24.1 Tue 9:30 EW 202

High-throughput exploration of alloying as design strategy for thermoelectrics — •Sandip Bhattacharya and Georg Madsen — ICAMS, Ruhr-Universität Bochum, Germany

The quintessential salient features of a modern thermoelectric material must be, large energy conversion efficiencies and that they must be comprised of economical and innocuous constituents. Along these lines, we will discuss a new materials design strategy based on Vegard's law to optimize the thermoelectric figure of merit, zT, in binary alloys. Using a combinatorial high-throughput formalism we have explored 300 different binary M-X(X') systems, where M is a Group 1-12 element while X (X') is Si, Ge or Sn. We have identified eight promising candidates that are constituted by non-toxic and inexpensive elements and have the potential of a high zT, in addition to being thermodynamically stable. For the candidates, we shall also explore in detail the correlation between their electronic structures and thermoelectric properties, to understand the source of enhancement in their transport characteristics. Furthermore, we will discuss the descriptors used to quantify the improved thermoelectric performance and their ease of alloy formation.

HL 24.2 Tue 9:45 EW 202

Density functional calculations of the thermoelectric properties of ZrNiSn and ZrCoBi — •Gregor Fiedler and Peter Kratzer — Faculty of Physics, University Duisburg-Essen, 47048 Duisburg, Germany

Finding "green", inexpensive and efficient materials combinations for thermoelectric energy harvesting is a challenge. We have conducted a theoretical study of ZrCoBi, ZrNiSn and their heterostructures for thermoelectric applications. We present results from first-principles calculations for all factors contributing to the figure of merit ZT. Using density functional theory, we compute the electronic and phononic spectrum, deformation potentials and elastic constants. From the electronic band structure, the Seebeck coefficient and the electronic conductivity are calculated. For the latter, acoustic intravalley scattering is included using the calculated deformation potentials. Moreover, we show that disordered and off-stoichiometric materials display defects states in the band gap. The unavoidable occurrence of these defects due to their low formation energy is responsible for the very small band gap in ZrNiSn reported experimentally, and the high thermal carrier concentration. In heterostructures of ZrNiSn and ZrCoBi, the thermal conductivity is predicted to be substantially reduced. We estimate this reduction using the diffuse mismatch model based on the calculated phonon spectra, including optical phonons.

HL 24.3 Tue 10:00 EW 202

First principles calculations of point defects to optimize the thermoelectric efficiency of half-Heusler compounds. — •Robin Stern and Georg Madsen — Ruhr-Universität Bochum, ICAMS

In future, thermoelectric materials can play a significant role in enhanced energy efficiency. The thermoelectric performance of a material is determined by the power-factor, $S^2\sigma$ and the thermal conductivity κ. Half-Heusler compounds, consisting of three interpenetrating fcc sublattices, are an interesting class of materials, since they exhibit a relatively large Seebeck coefficient S. Furthermore, each sublattice can be doped independently to increase the power-factor and lower the thermal conductivity. The power-factor is strongly influenced by the carrier concentration. We used DFT point-defect calculations to evaluate the defect formation energies of various dopants and studied the influence on the carrier concentration. Using the example of NiTiSn, we discuss how the growth conditions of the half-Heusler compound influences the intrinsic carrier concentration and how extrinsic doping can significantly increase the latter.

HL 24.4 Tue 10:15 EW 202

Formation and function of vacancies in Si/Ge Clathrates: The importance of broken symmetries — •Amrita Bhattacharya, Christian Carbogno, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

One promising material class for improved thermoelectrics are the clathrates, i.e., semiconducting host lattices encapsulating guest atoms. Even in simple clathrates, such as, Si_{46} and Ge_{46}, the introduction of guests can result in important but not yet understood effects: In Si hosts, the addition of K (or Ba) results in defect-free K_8Si_{46} (Ba_8Si_{46}) phases. In spite of their structural and electronic similitude, Ge hosts behave fundamentally different upon filling: Under addition of K/Ba, the most stable phases are K_8Ge_{44} and Ba_8Ge_{43}, having *two* and *three* tetravalent framework vacancies respectively that completely/ partially balance the electrons donated by the guests. In this work, we use density-functional theory, carefully evaluating the role of exchange correlation functionals, to compute the formation energies of vacancies and vacancy complexes in Si- and Ge-hosts as function of the filling with K/Ba. By taking into account structural disorder, geometric relaxations, and vibrational entropies, we verify and explain the experimentally found vacancy concentration and the thermodynamic stabilities of these compounds. We can trace back the contrasting behavior of Si/Ge clathrates upon filling to a curious, charged vacancy induced break in symmetry that occurs in Si but not in Ge hosts.

HL 24.5 Tue 10:30 EW 202

Chemical ordering in inorganic clathrates and its effect of thermoelectric performance — •Paul Erhart, Mattias Ångqvist, and Daniel Lindroth — Chalmers University of Technology, Gothenburg, Sweden

Inorganic clathrates are of interest due their very good thermoelectric performance at elevated temperatures. Here, we consider type-I clathrates with composition $A_8B_{16}C_{30}$, where A=Ba is the guest species while B=Al/Ga and C=Si/Ge comprise the matrix. Cluster expansions and Monte Carlo simulations are employed to explore chemical ordering in these materials. The cluster expansion models are parametrized with respect to density functional theory calculations using a compressive sampling approach. The calculated site occupancy factors are in very good agreement with experiment. The Al-Al and Ga-Ga nearest neighbor pair interaction is always repulsive, which is in accord with the empirical rule that Al-Al/Ga-Ga pairs are to be avoided. Using Boltzmann transport theory we then quantify the effect of chemical order on the electrical and thermal conductivity as well as the Seebeck coefficient. The results are discussed with respect to their implications on thermoelectric performance and the potential for property modification via controlling the degree of order in the system.

HL 24.6 Tue 10:45 EW 202

Thermoelectric properties of n-doped Silicon and Copper from first-principles — •Mattia Fiorentini and Nicola Bonini — King's College London, Strand, London, United Kingdom

Understanding transport phenomena is a key task to design and engineer materials for thermoelectric and nano-electronic applications. Despite the extensive activity in the field, the state-of-the-art still lacks a comprehensive first-principles numerical framework to tackle the problem. Here we present a computational infrastructure to calculate the electronic transport coefficients of bulk systems within the Boltzmann transport equation (BTE) formalism. The electronic and vibrational properties, including the electron-phonon interaction, are computed using Density Functional theory and Density Functional Perturbation theory. We exploit the Wannier interpolation to efficiently sample fine grids in reciprocal space. The linearized BTE is solved exactly using a Conjugate Gradient algorithm. Our method goes beyond the standard practice, which relies upon various flavors of the relaxation-time approximation and uses semi-empirical models of carriers' dispersions and interactions. Here we study the thermoelectric properties of n-doped Silicon and Copper in a wide range of temperatures. Our results are in good agreement with the experimental observations and elucidate the relative importance of the various scattering mechanisms in the different regimes. For Copper, we give an explanation for the anomalous behavior of the Seebeck coefficient. As an additional outcome, we assess the accuracy of simplified models and approximations that are commonly used to study transport in semiconductors.

HL 24.7 Tue 11:00 EW 202

Achieving optimum carrier concentrations in p-doped SnS thermoelectrics — •Sandip Bhattacharya[1], Naga Harsha Gunda[1], Robin Stern[1], Gilles Dennler[2], and Georg Madsen[1] — [1]ICAMS, Ruhr-Universität Bochum, Germany — [2]IMRA Europe

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SnS is a commercially viable and environmentally friendly thermoelectric material. Recently [1] it was shown from an intermediate throughput investigation that p-doping in SnS can be achieved effectively with monovalent cations. This improves the itinerant carrier's concentration thereby enhancing its powerfactor. In particular, Ag-doped SnS under Sulphur rich environment showed encouraging transport properties. We shall elaborate upon our previous work and explore the possibility of p-doping SnS with Ag, Li, Cu, Na and K. We will discuss the effects of two ubiquitous effects that can result in decreasing the hole concentration. These undesired phenomena include the formation of coupled defects and oxidation of the dopant. This work serves as a comprehensive guide to achieve an efficient p-doped SnS thermoelectric material. [1] C. Bera, et al, Phys.Chem. Chem. Phys. 16, 19894 (2014).

Coffee break

HL 24.8 Tue 11:30 EW 202

Resistance Fluctuation Spectroscopy on Thermoelectric $CoSb_3$ and Partially Filled $Yb_xCo_4Sb_{12}$ Skutterudites — •Sven Heinz[1], Martin Lonsky[1], Marcus Daniel[2], Manfred Albrecht[2,3], and Jens Müller[1] — [1]Physikalisches Institut, Goethe-Universität, Frankfurt (M), Germany — [2]Institut für Physik, TU Chemnitz, Chemnitz, Germany — [3]Institut für Physik, Universität Augsburg, Augsburg, Germany

Thermoelectric materials can directly convert heat to electricity. For the efficiency of this conversion to be high, materials have to have a high electrical conductivity and a low thermal conductivity. Pure $CoSb_3$ combines these conflicting properties unusually well. Thermal conductivity can be further reduced by introducing so called "rattling atoms" that can move relatively freely at interstitial sites, therefore acting as very efficient scattering centers for phonons. We studied how the introduction of Ytterbium as rattling atoms in $CoSb_3$ alters its electronic transport properties. Besides standard transport measurements, like resistivity and hall-effect measurments, resistance fluctuation spectroscopy has been performed. While $1/f$-type-noise dominates in the unfilled samples, we found unusually strong Lorentzian spectra and random telegraph noise in the Ytterbium-filled samples and determined characteristic activation energies of the underlying switching processes. The activation energies E_a exhibit a characteristic temperature dependence, i.e. E_a increases from values of about 5 meV at low temperatures to values of up to 250 meV near room temperature, which is close to the gap energy for the pure material.

HL 24.9 Tue 11:45 EW 202

Thermoelectrics of mesoscopic transport influenced by an electromagnetic environment — •Michael Mecklenburg, Björn Kubala, and Joachim Ankerhold — University Ulm, Institut for Complex Quantum Systems (ICQ), Albert-Einstein-Allee 11, D-89069 Ulm, Germany

Mesoscopic systems have been considered as interesting candidates for thermoelectric applications. This is due to strong energy-dependent transport features, as shown, for instance, in resonant tunneling through a quantum dot. Transport through such a quantum system is also influenced by the electromagnetic properties of the circuit into which it is embedded. Such effects on thermoelectric properties have, so far, received only scant attention [1].
Here, we apply P(E)-theory to investigate the impact of different types of electromagnetic environment on the thermopower. Introducing a strong asymmetry into the system allows for a controlled tuning of the effective temperature bias. Extensions beyond the single-dot case considered here are possible.

[1] T. Ruokola und T. Ojanen, Phys. Rev. B, **86** (2012), 035454.

HL 24.10 Tue 12:00 EW 202

Bound on Thermoelectric Power in a Magnetic Field — •Kay Brandner and Udo Seifert — II. Institut für Theoretische Physik, Universität Stuttgart, 70550 Stuttgart, Germany

Strong numerical evidence for the existence of a so far undiscovered constraint on the Onsager coefficients describing thermoelectric transport in the presence of a magnetic field is presented on the basis of the paradigmatic n-terminal model with n-2 terminals acting as probes mimicking correlations and inelastic scattering. The new constraint implies, inter alia, that power vanishes at least linearly when the maximum efficiency is approached. This result goes beyond the bounds discussed in our previous work [1,2], since, first, it holds for an arbitrarily large number of terminals and, second, power is bounded rather than efficiency. In particular the option of reaching Carnot efficiency at finite power, which, in principle, would be allowed by the bare second law, is finally ruled out for the multi-terminal set-up.

[1] K. Brandner, K. Saito and U. Seifert, Phys. Rev. Lett. **110** 070603 (2013)
[2] K. Brandner and U. Seifert, New J. Phys. **15** 105003 (2013)

HL 24.11 Tue 12:15 EW 202

Quantum Nernst engines — •Björn Sothmann[1], Rafael Sánchez[2], and Andrew N. Jordan[3] — [1]Département de Physique Théorique, Université de Genève, Genève, Switzerland — [2]Instituto de Ciencia de Materiales de Madrid, CSIC, 28049, Madrid, Spain — [3]Department of Physics and Astronomy, University of Rochester, Rochester, USA

Recently, there has been a growing interest in quantum heat engines with broken time-reversal symmetry as such systems in principle allow for increased efficiencies [1]. Here, as a concrete example of such a setup, we consider a quantum Nernst engines based on edge states in the quantum Hall regime [2]. We identify a geometry that exhibits an extreme asymmetry between the off-diagonal Onsager coefficients for heat and charge transports. In terms of thermodynamic efficiency, this engine outperforms a recently proposed classical Nernst engine [3]. A second setup using an antidot is found to be more efficient as energy filtering becomes less strong; a behaviour in stark contrast to other heat engines.

[1] K. Brandner, U. Seifert, New J. Phys. **15**, 105003 (2013).
[1] B. Sothmann, R. Sánchez, A. N. Jordan, EPL **107**, 47003 (2014).
[2] J. Stark, K. Brandner, K. Saito, U. Seifert, Phys. Rev. Lett. **112**, 140601 (2014).

HL 24.12 Tue 12:30 EW 202

Quantum Hall thermoelectrics — •Rafael Sánchez[1], Björn Sothmann[2], and Andrew N. Jordan[3,4] — [1]Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain — [2]Département de Physique Théorique, Université de Genève, Switzerland — [3]Department of Physics and Astronomy, University of Rochester, U.S.A. — [4]Institute for Quantum Studies, Chapman University, U.S.A.

In an electronic circuit, current can be generated by the conversion of heat absorbed from a hot region. In the absence of a magnetic field, such thermoelectric response requires broken left-right and particle-hole symmetries. We investigate the thermoelectric properties of a three-terminal quantum Hall conductor. We identify a contribution to the thermoelectric response that relies on the chirality of the carrier motion rather than on spatial asymmetries [1]. The Onsager matrix becomes maximally asymmetric with configurations where either the Seebeck or the Peltier coefficients are zero while the other one remains finite. Reversing the magnetic field direction exchanges these effects. Our results show that thermoelectric measurements are sensitive to the chiral nature of the quantum Hall edge states, opening the way to control quantum coherent heat flows. In particular, powerful and efficient energy harvesters can be proposed [1,2]. The possibility to generate spin-polarized currents in quantum spin Hall samples is also discussed.

[1] R. Sánchez, A. N. Jordan, B. Sothmann, arXiv:1410.6639.
[2] B. Sothmann, R. Sánchez, A. N. Jordan, EPL 107 47003 (2014).

HL 24.13 Tue 12:45 EW 202

Use of resonant tunneling to enhance low dimensional thermoelectric performance — •Bhaskaran Muralidharan and Akshay Agarwal — Department of Electrical Engineering, IIT Bombay, Powai, Mumbai-400076, India

Low-dimensional systems with sharp features in the density of states have been proposed as a means to improving the efficiency of thermoelectric devices. Quantum dot systems, which offer the sharpest density of states achievable, however, suffer from low power outputs while bulk (3-D) thermoelectrics, while displaying high power outputs, offer very low efficiencies. Here, we analyze the use of a resonant tunneling diode structure that combines the best of both aspects, that is, density of states distortion with a finite bandwidth due to confinement that aids the efficiency and a large number of current carrying trans-

verse modes that enhances the total power output [1]. We show that this device can achieve a high power output at efficiencies close to 40% of the Carnot efficiency due to the contribution from these transverse momentum states at a finite bandwidth. We then provide a detailed analysis of the physics of charge and heat transport with insights on parasitic currents that reduce the efficiency.

[1] A. Agarwal and B. Muralidharan, Appl. Phys. Lett., 105, 013104, (2014).