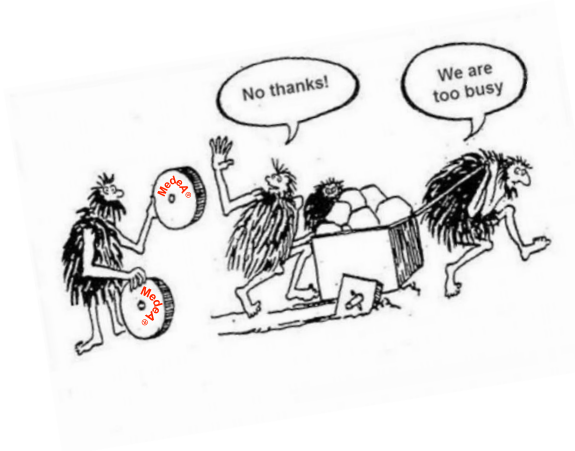




materials design®

The MedeA® Software Platform: Overview and Applications



Volker Eyert and Malin Sohlmér

Materials Design Inc.

Thermoelectric Network Meeting
Reading
11-12 November 2015

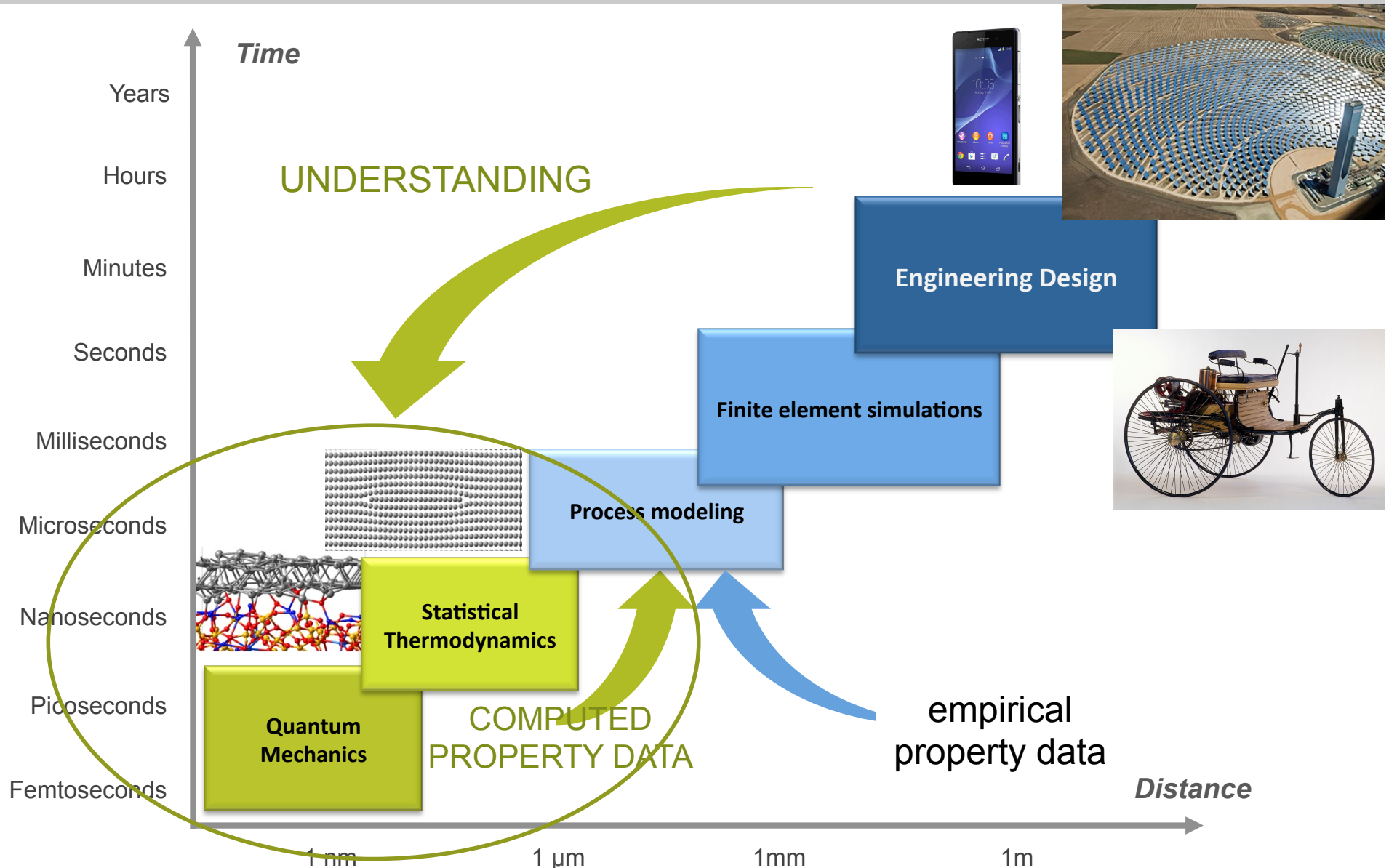


Agenda

- ▶ Company Profile Materials Design
 - Products and Services: Software and Consulting
- ▶ Challenges and Solutions
 - Capabilities of the MedeA[®] software environment
- ▶ Selected Applications
 - Electronic properties
 - Phonon dispersions
 - Transport properties
- ▶ Discussion and Software Demonstration



Technology Positioning

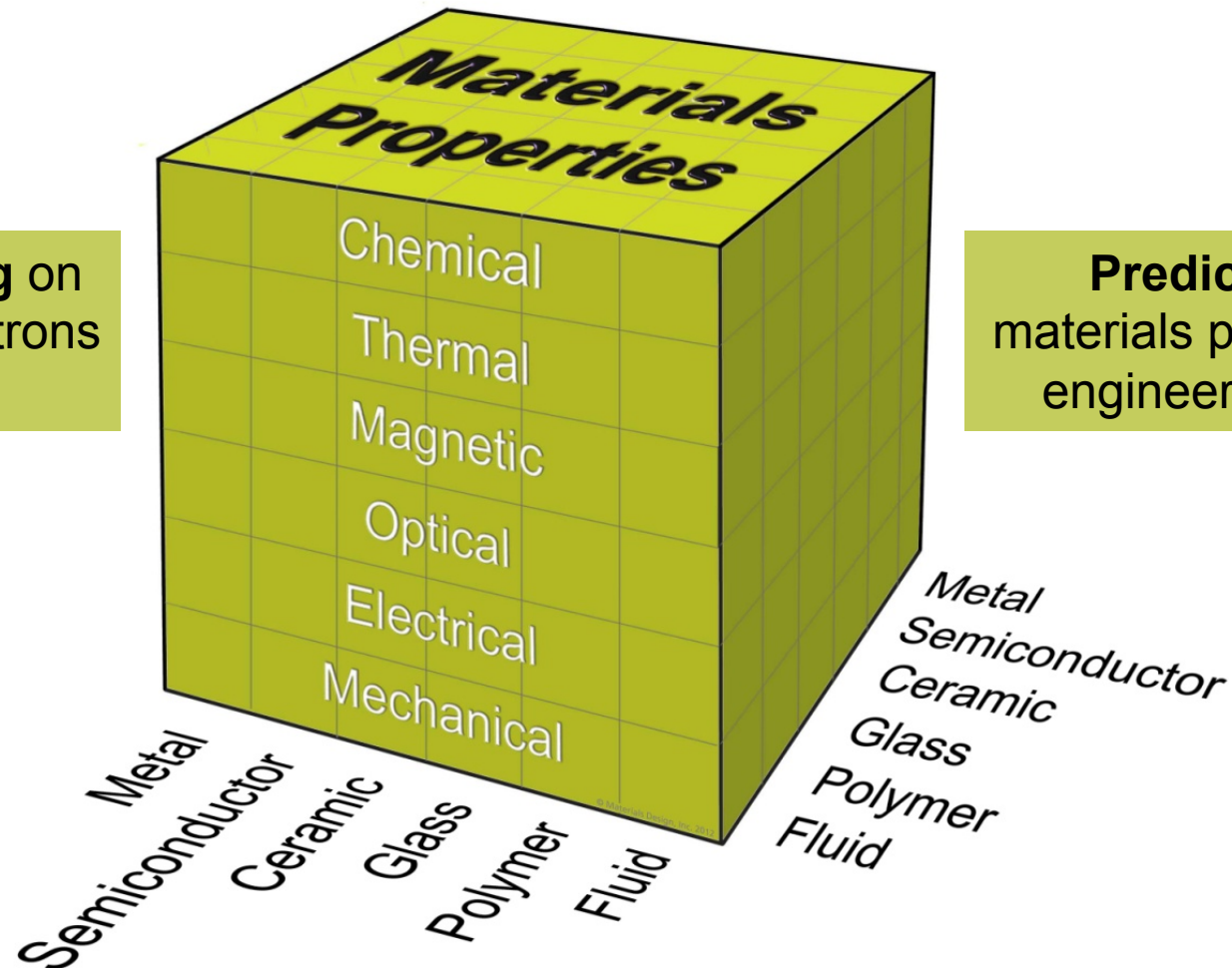




Goal of Atomistic Simulations

MedeA[®]: Software for Efficient R&D

Understanding on the level of electrons and atoms



Prediction of materials properties of engineering value



materials design

Company Profile

- ▶ Founded by scientists in 1998
- ▶ Over 400 customers in industry, universities, and government laboratories including over 50 major companies worldwide
- ▶ Products: **MedeA**[®] software, support, and consulting services
- ▶ Global: Offices in San Diego, Angel Fire, Paris, and Stockholm
- ▶ Business partners: Japan, Korea, China, Taiwan, Singapore, and India
- ▶ Core competence in
 - Computational chemistry & physics
 - Materials science & chemical engineering
 - Materials property databases & software engineering



Products and Services

▶ MedeA[®] software

- Comprehensive atomistic modeling environment with leading technology
- Installation, training, online support, and maintenance
- Scientific/technological interactions
- Users group meetings

▶ Contract research

- Solution of specific industrial problems
- Leverages expertise and resources of MD's scientists
- Publicly funded programs

▶ Technology partnerships

- Development of customized modeling capabilities (e.g. Toyota)





Customers

Energy

Metals &
Alloys

Chemicals

Oil & Gas

Electronics

Automotive &
Aerospace

Glass &
Ceramics

Mining &
Drilling

Universities and Government R&D Laboratories



Materials Exploration and Design Analysis



MedeA[®] Software



MODELING & ANALYSIS

Builders: crystals, defects, interfaces, surfaces, molecules, nanostructures, polymers, amorphous materials

Analysis: geometry, band structures and DOS, electron and spin density, potential, Fermi surface, phonons, transition states, dynamics trajectories

Job Server

DATABASES

Experimental and Computed Structure and Property Data

ICSD

NIST Crystal Data

Pauling

Pearson

Computed

Task Servers

Mechanical

Thermal

Chemical

Kinetic

Electric

Optic

Magnetic

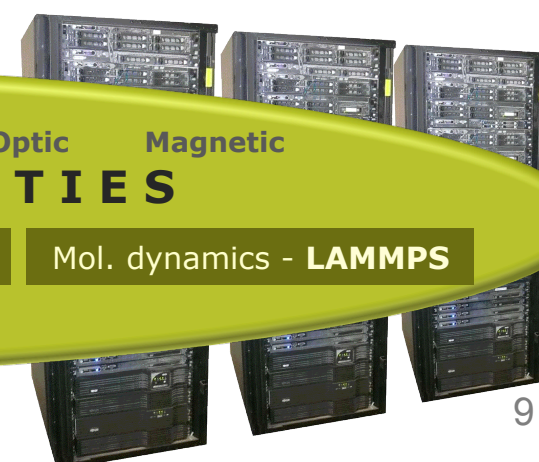
COMPUTATION OF PROPERTIES

ab initio QM - **VASP**

Semi-empirical - **MOPAC**

Monte Carlo - **GIBBS**

Mol. dynamics - **LAMMPS**





MedeA[®] Components

▶ MedeA[®]-Environment

- Model builders
- Database infrastructure
- Analysis tools
- Flowcharts
- JobServer/TaskServer

▶ InfoMaticA

- About 500,000 database entries combining ICSD, Pearson, Pauling, NIST Crystal Data, COD
- Computed data

▶ VASP

- GGA , post-DFT (hybrid, sX, GW, RPA)
- H to Cm PAW potentials (all electron)
- Spin-orbit relativistic
- Linear response

▶ LAMMPS

- Forcefields including pcff+, ionic, EAM

▶ GIBBS

- Adsorption
- Fluid phase equilibria

▶ MOPAC

- Semi-empirical QM, PM7
- Thermodynamics, IR, UV-vis

Property Packages

▶ Mechanical-Thermal (MT)

▶ Phonon

- Phonon dispersions
- Vibrational properties
- Thermodynamic functions

▶ Electronics

- Effective masses
- Boltzmann transport
- Electrical/thermal conductivity
- Thermoelectricity

▶ Transport

- Diffusion
- Thermal conductivity
- Viscosity

▶ Transition State (TSS)

▶ Amorphous materials

▶ Polymer properties

- QSPR

▶ PrediBond[™] – catalysis

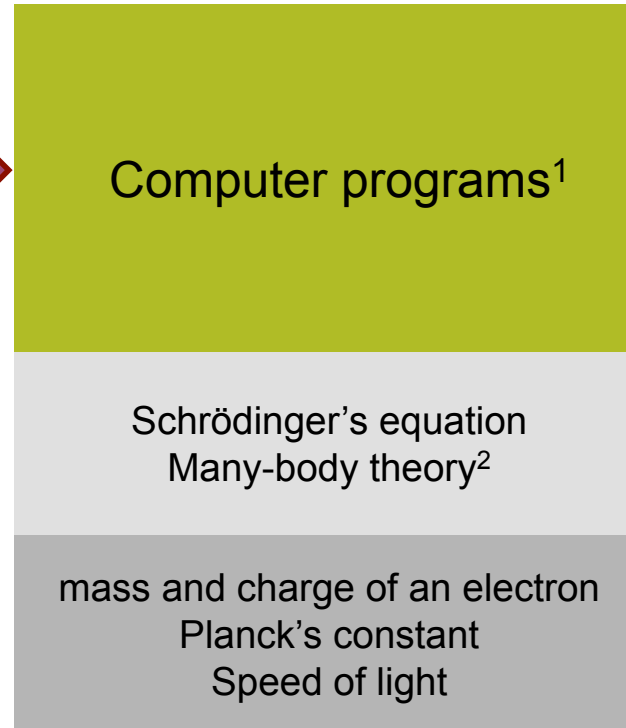


Ab Initio Methods

INPUT

- ▶ Arbitrary position of atomic nuclei
- ▶ Atomic numbers
- ▶ Atomic masses

$$\mathbf{H}\Psi = E\Psi$$



OUTPUT

- ▶ Interatomic distances
- ▶ Lattice parameters
- ▶ Stress
- ▶ Thermodynamic stability
- ▶ Defect energies
- ▶ Surface energies
- ▶ Grain boundary energies
- ▶ Adsorption energies
- ▶ Binding energies of impurities
- ▶ Reaction barriers
- ▶ Diffusion rates
- ▶ Electronic, optic, and magnetic properties
- ▶ ...

1. Vienna Ab initio Simulation Package (VASP)
2. Density functional theory (DFT)

- free of system-specific parameters
- general and high predictive power
- few hundred atoms per simulation box
- very short time scales (pico-seconds)



Forcefield Methods

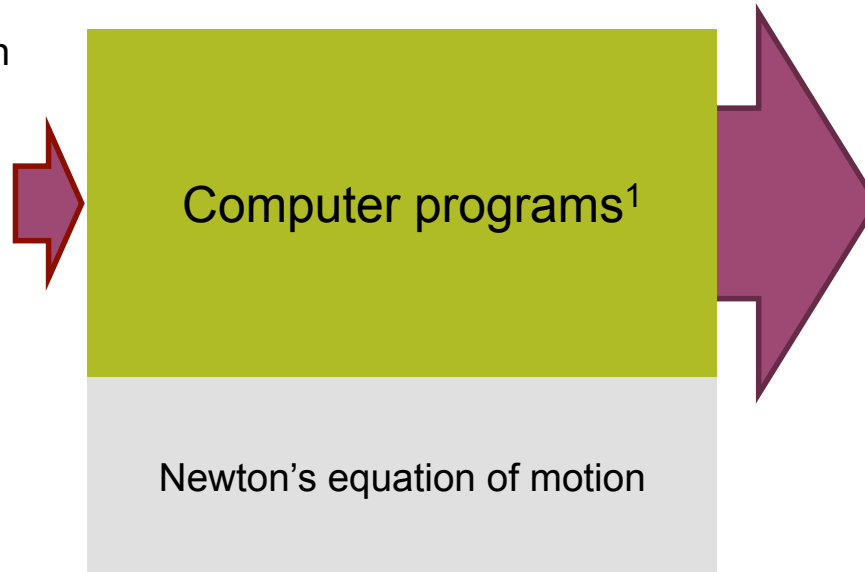
INPUT

- ▶ Arbitrary position of atomic nuclei
- ▶ Atom types
- ▶ Atomic masses
- ▶ Parameters for interatomic interactions

$$F = m \frac{\partial^2 E}{\partial x^2}$$

$$E = \sum_{i,j} V_{bonds}(r_{ij}) + \sum_{i,j,k} V_{angles}(\theta_{ijk}) + \dots$$

1. Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)



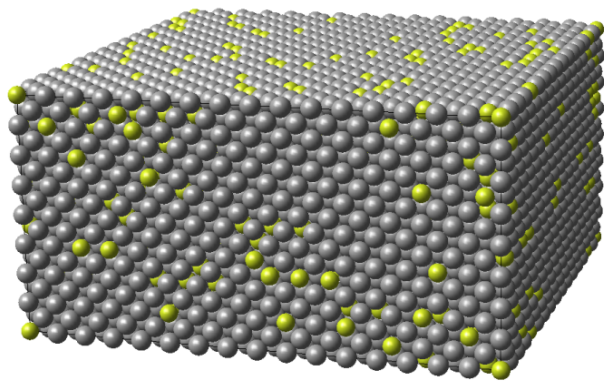
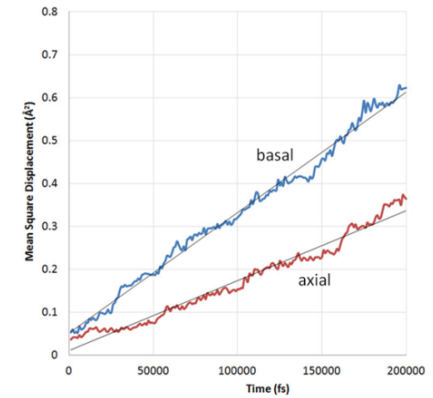
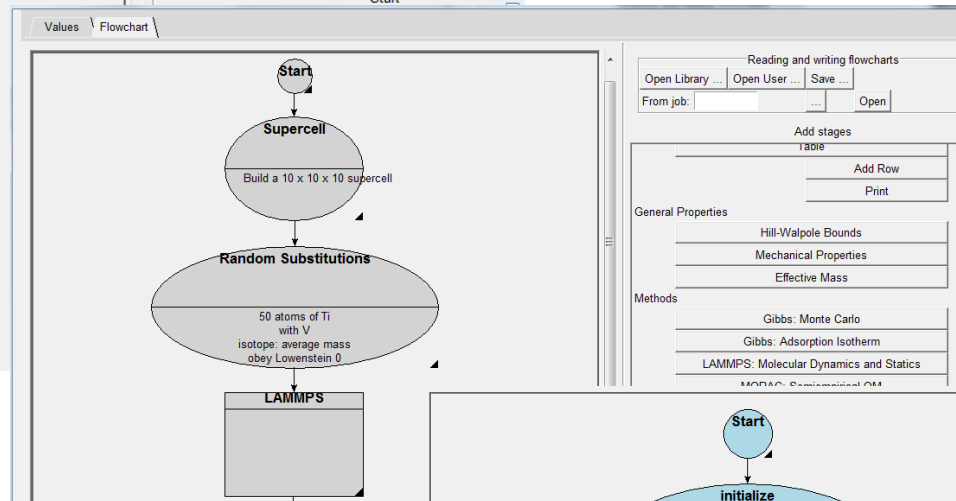
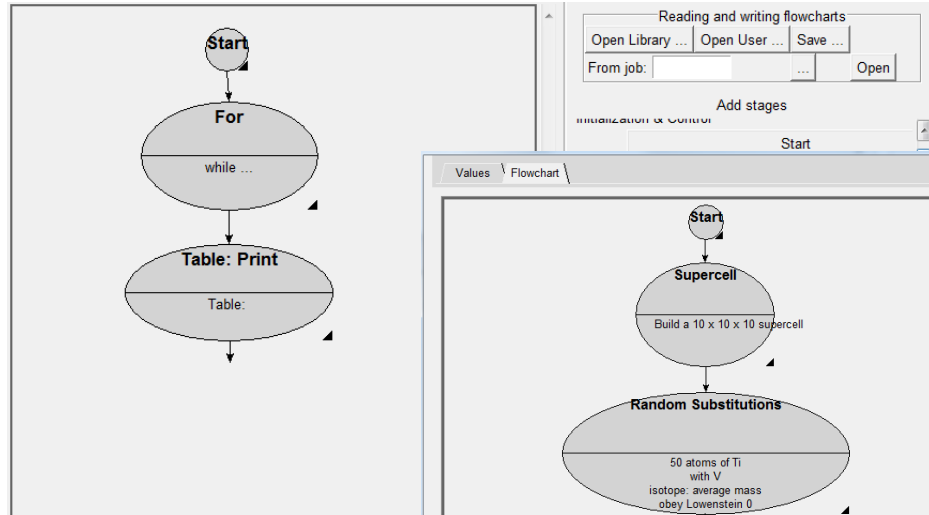
OUTPUT

- ▶ Interatomic distances
- ▶ Lattice parameters
- ▶ Stress
- ▶ Thermodynamic stability
- ▶ Defect energies
- ▶ Dislocations
- ▶ Surface energies
- ▶ Grain boundary energies
- ▶ Diffusion rates
- ▶ ...

- system-specific parameters fitted to ab initio or experimental data (MedeA[®]-FFO)
- predictive within range of fitting parameters
- up to millions of atoms per simulation box
- time scales into the nano-seconds
- no electronic structure-related properties



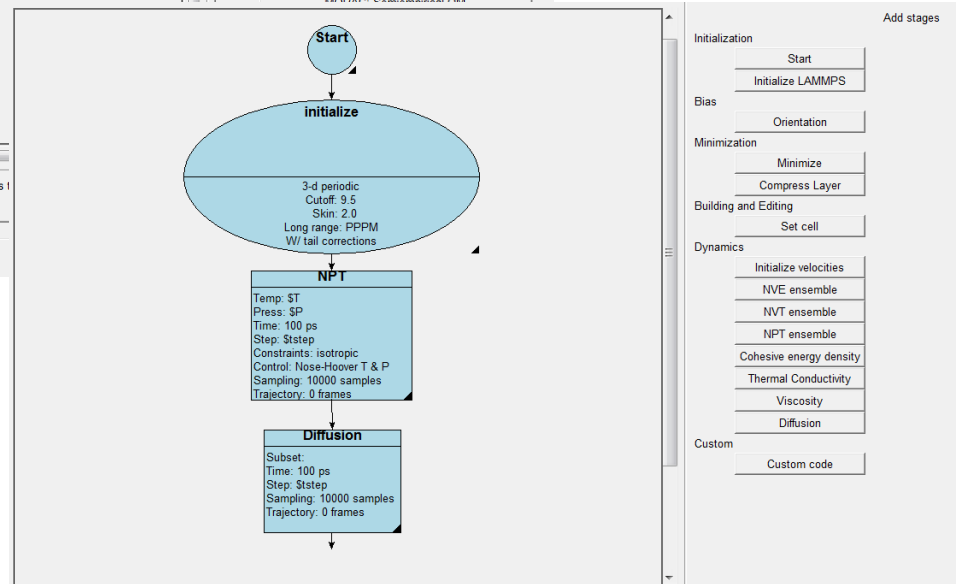
Flowcharts



Maximum number of jobs 1

while ...

OK

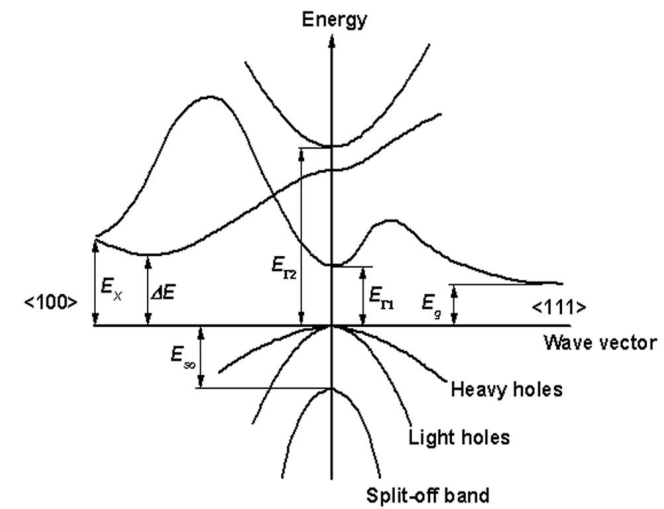
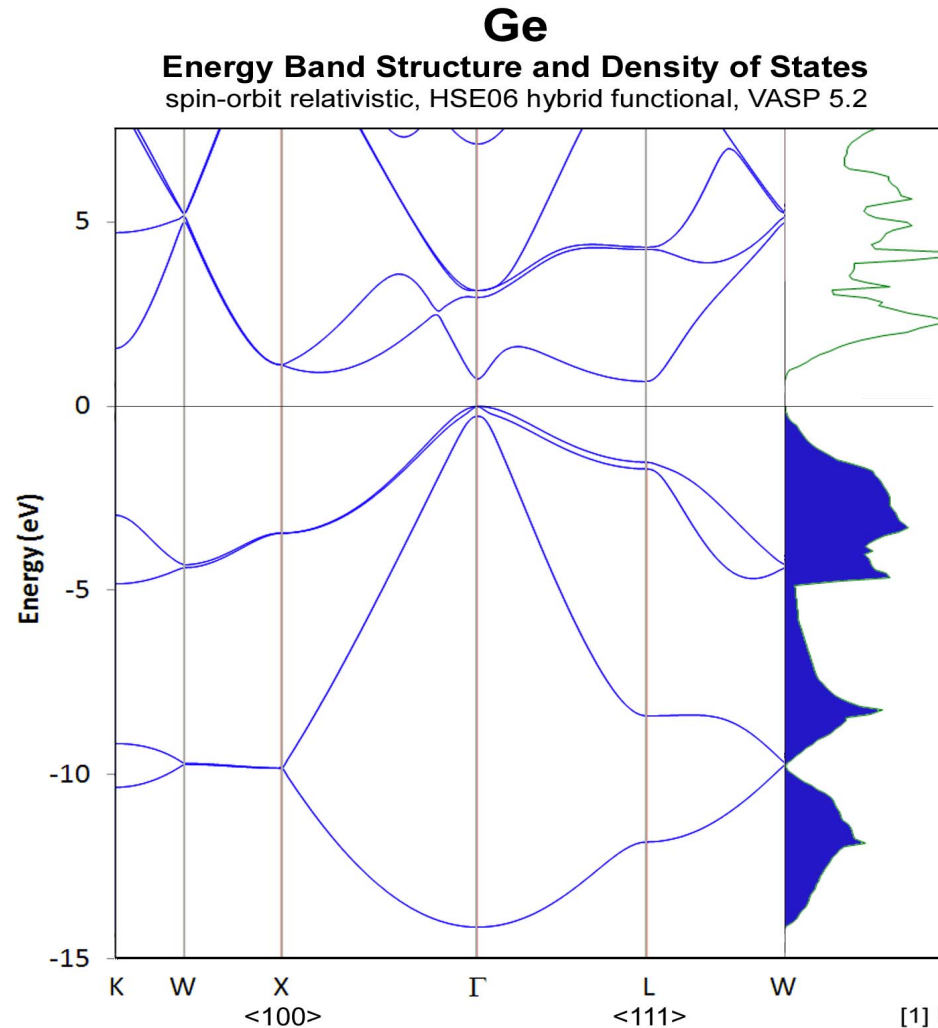




Electronic Properties, Band Gaps



Accurate Band Structures



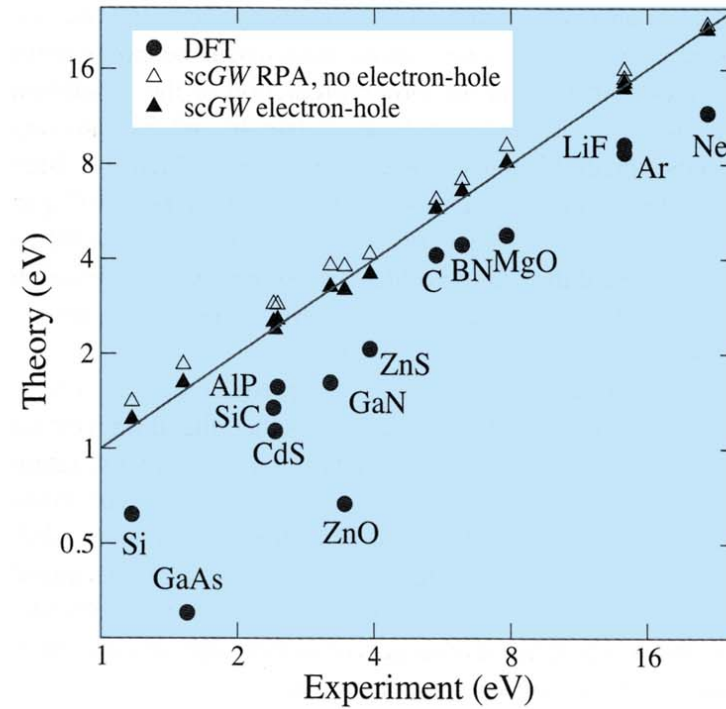
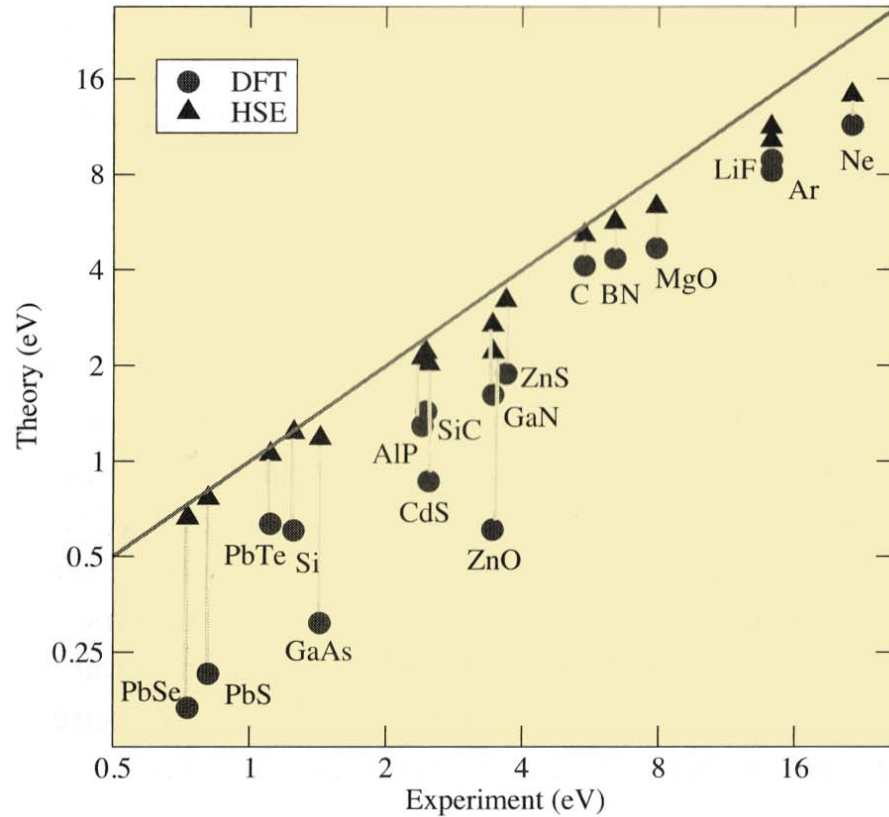
	Expt. [1]	Computed
300 K	$E_g = 0.66$ eV	0.66
	$E_x = 1.2$ eV	1.12
	$E_{R1} = 0.8$ eV	0.73
	$E_{R2} = 3.22$ eV	3.14
	$\Delta E = 0.85$ eV	0.91
	$E_{so} = 0.29$ eV	0.29

[1] <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/Ge/bandstr.html>

Note: Standard LDA or GGA predicts Ge to be metallic



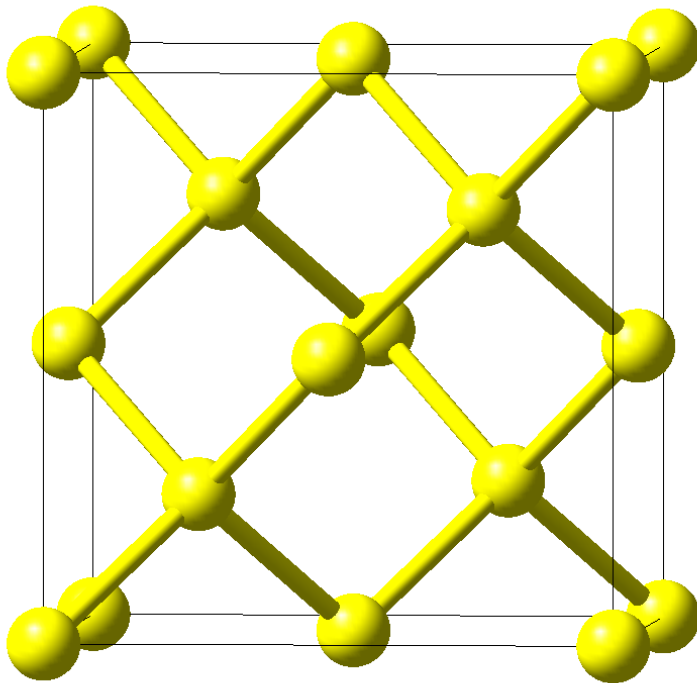
Accuracy of Computed Band Gaps



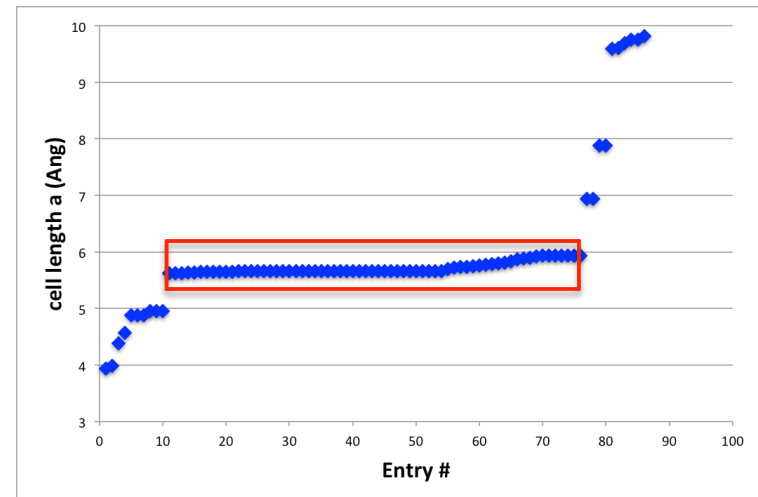
Performance of VASP 5.2 as reviewed by
J. Hafner, J. Phys.: Cond. Matter **22**, 384205 (2010)



Germanium: Atomic Structure



- cubic, space group Fd-3m
- $a_{\text{comp}} = 5.671 \text{ \AA}$
- $a_{\text{exp}} \approx 5.658 \text{ \AA}$ (Ioffe)
- $a_{\text{exp}} \approx 5.715 \text{ \AA}$ (InfoMaticA **ave**)



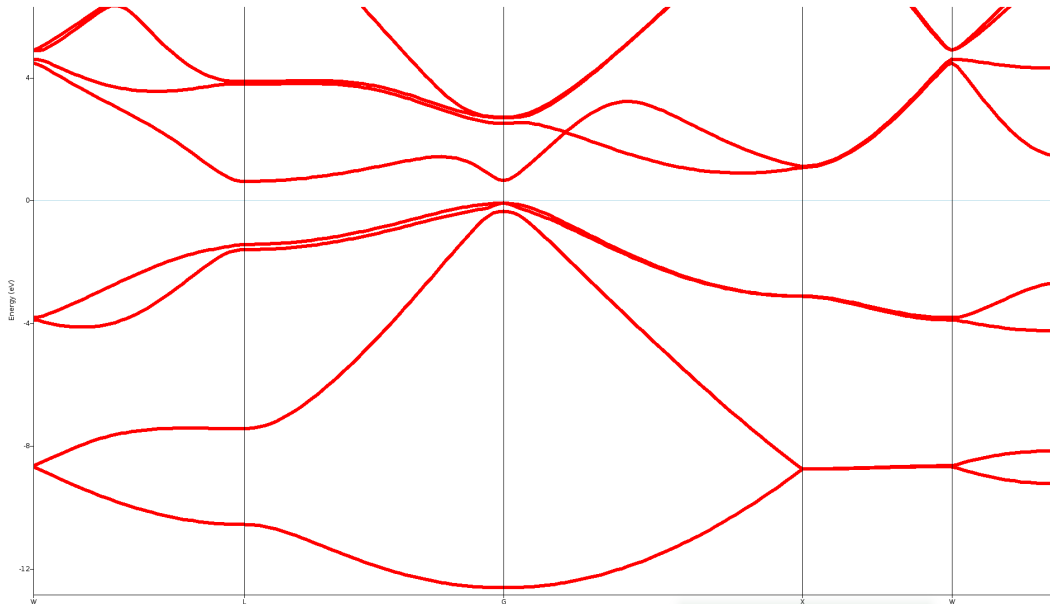
Ioffe: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>

Calculational parameters

- MedeA[®]-VASP 5.3
- PBEsol functional, spin-orbit relativistic
- standard 500 precision, reciprocal-space projection
- $\Delta\mathbf{k} \approx 0.2/\text{\AA}$, $11 \times 11 \times 11$ \mathbf{k} -points, Γ -centered



Germanium: Electronic Structure



Source	a (Å)	Gap (eV)
mBJLDA	5.658	0.72
mBJLDA	5.671	0.70
Ioffe	5.658 (300K)	0.66 (300K)
Ioffe		0.74 (0K)

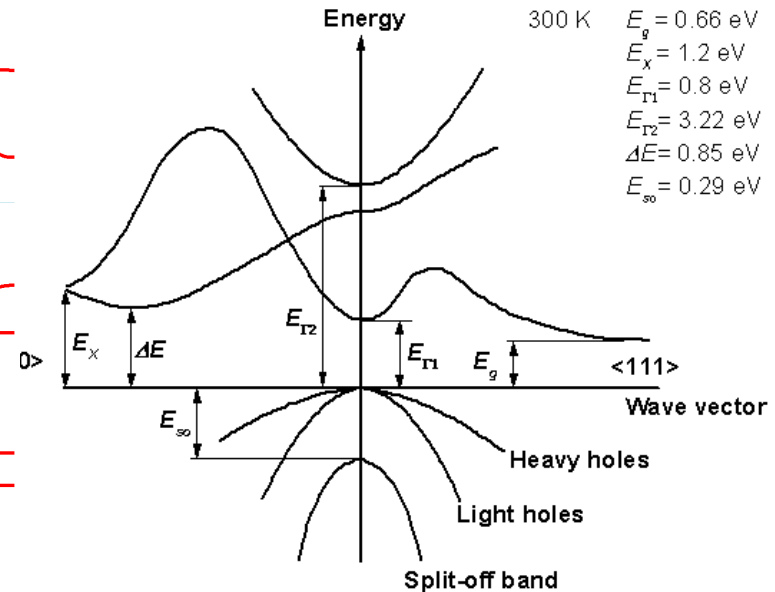
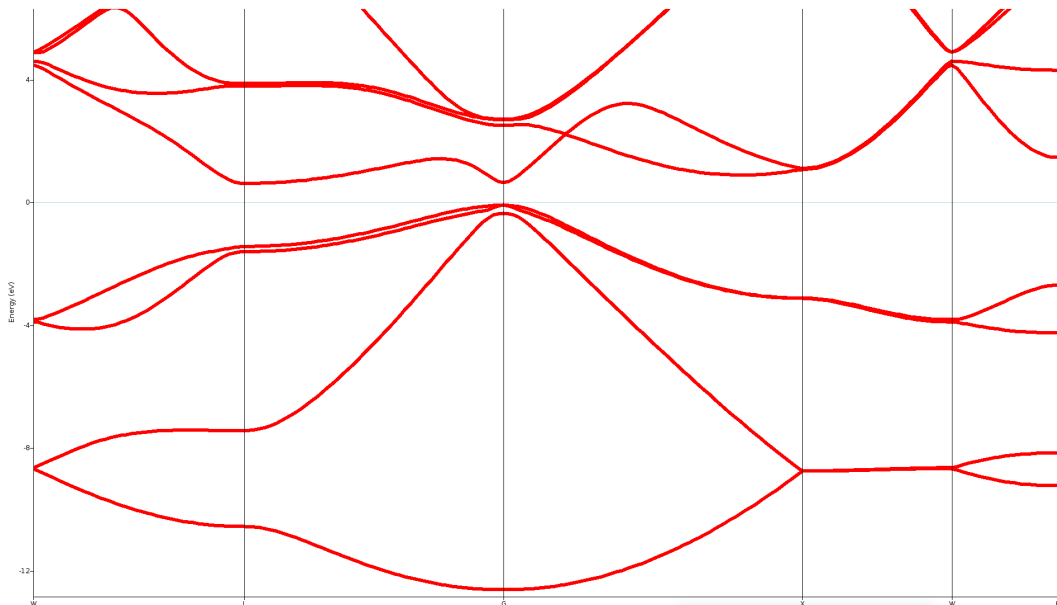
Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>
Handbook on Physical Properties of Semiconductors,
Vol. 2, ed. S. Adachi (Kluwer, Boston 2004)

Calculational parameters

- MedeA[®]-VASP 5.3
- mBJLDA functional, spin-orbit relativistic
- normal precision, default plane-wave cutoff
- reciprocal-space projection, linear tetrahedron method
- $\Delta\mathbf{k} \approx 0.2/\text{\AA}$, $11 \times 11 \times 11$ \mathbf{k} -points, Γ -centered



Germanium: Electronic Structure



Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>

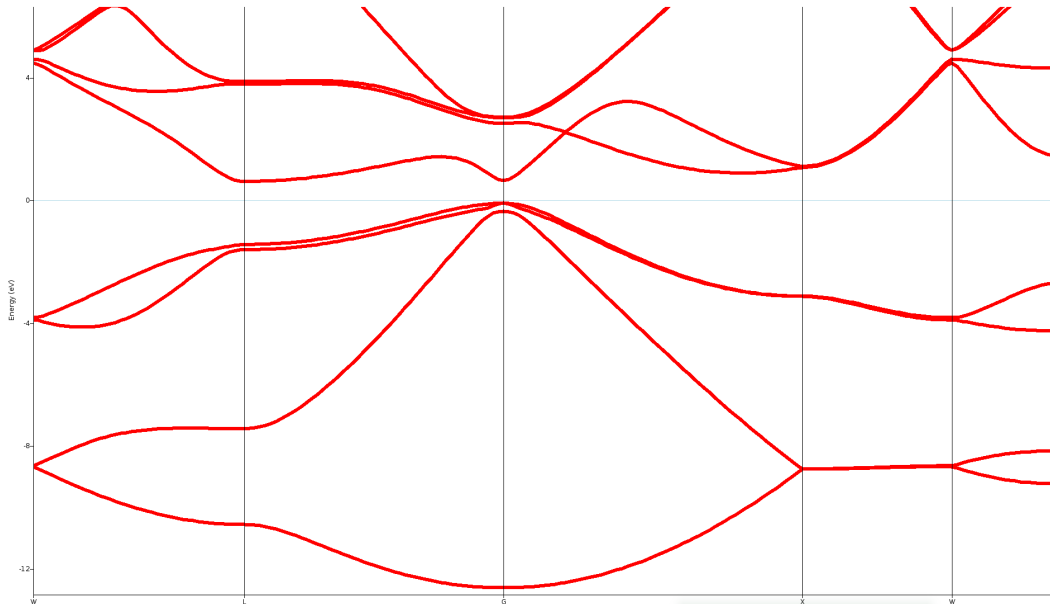
MedeA[®]-VASP

- computed band energies in good agreement with experimental data
- temperature effects (thermal expansion, phonons) may change the band structure

	Exp.	mBJLDA (5.658)	mBJLDA (5.671)
E_g	0.66	0.72	0.70
ΔE	0.85	0.95	0.98
E_x	1.12	1.15	1.15
E_{so}	0.29	0.27	0.27
E_{R1}	0.8	0.80	0.74
E_{R2}	3.22	2.78	2.78



Germanium: Effective Masses



MedeA[®]-Electronics

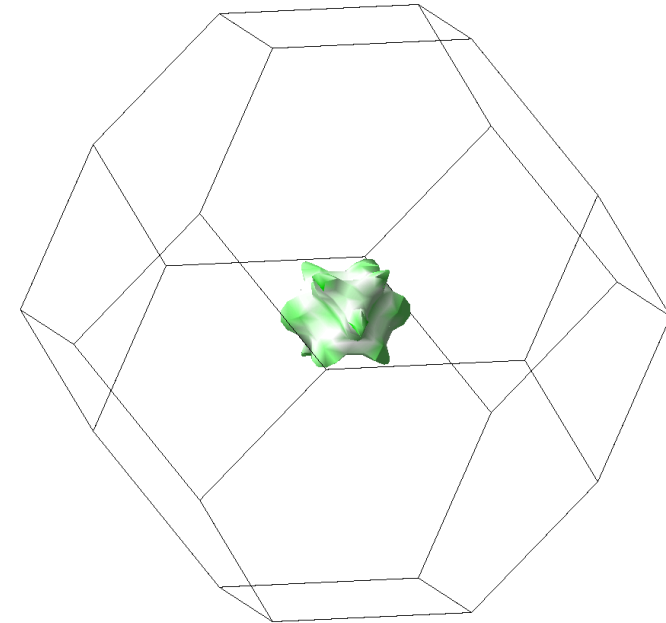
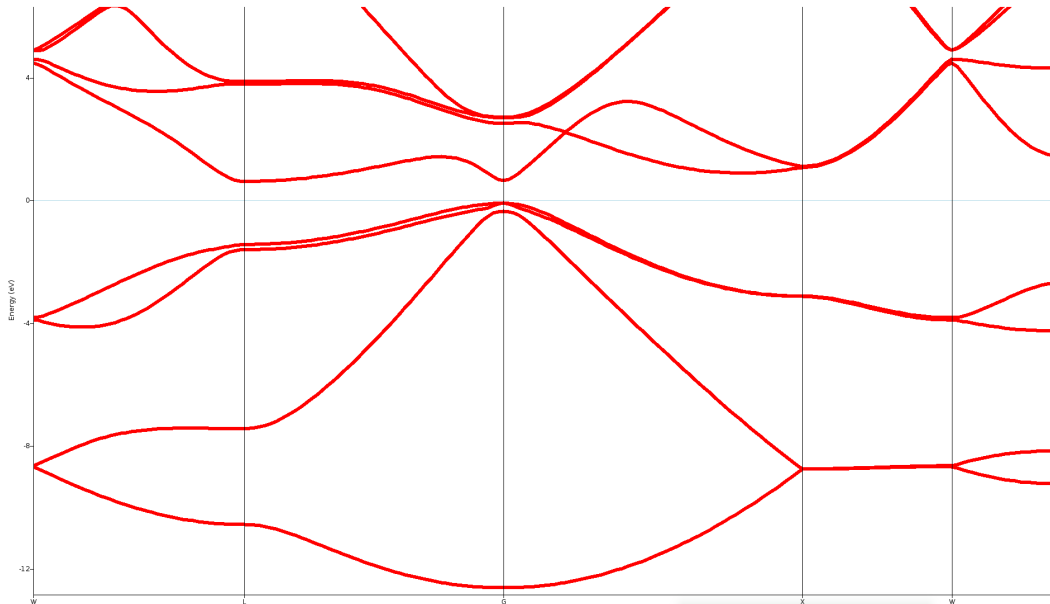
- computed effective masses in good agreement with experimental data
- heavy hole mass beyond parabolic approximation

	Exp.	MedeA
Electrons		
Long. Eff. Mass	1.59	1.77
Trans. Eff. Mass	0.081	0.096
DOS Mass	0.22	0.64
Conductivity Mass	0.12	0.14
Heavy Hole		
Eff. Mass	0.33	0.080
Light Hole		
Eff. Mass	0.043	0.085
Split-off band		
Eff. Mass	0.084	0.112

Exp.: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>



Germanium: Effective Masses



MedeA[®]-Electronics

- directional effective masses in reasonable agreement with **k•p** results

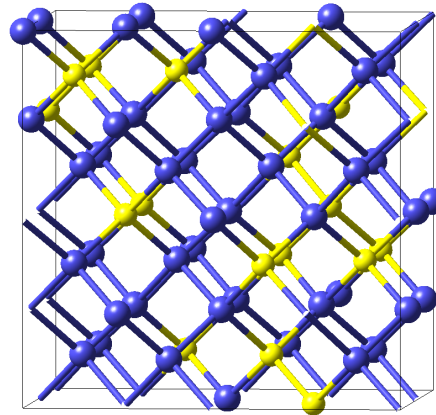
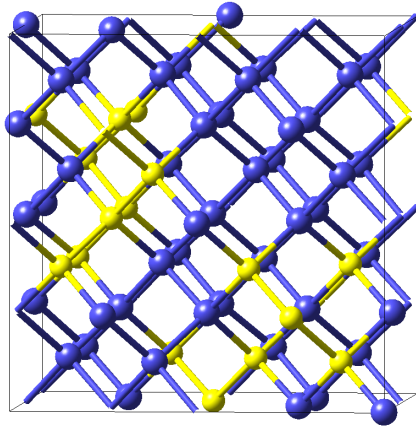
Directional effective masses:

	Heavy Hole			Light Hole		
	Exp.	k.p	calc	Exp.	k.p	calc
<001>	0.284	0.209	0.111	0.044	0.0459	0.066
<111>	0.376	0.503	0.561	0.043	0.0407	0.0455

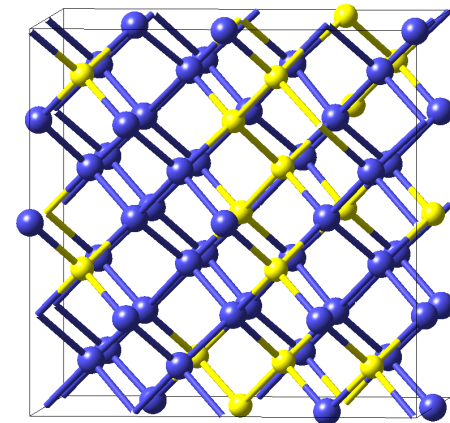
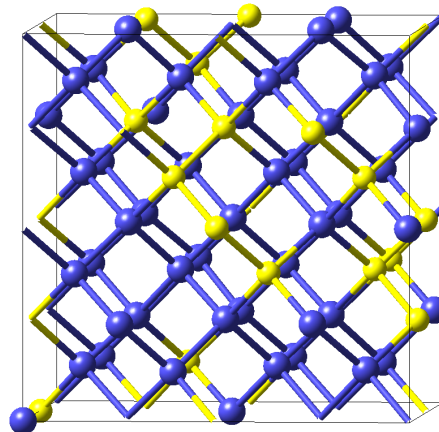
S. Ben Radhia *et al.*, J. Appl. Phys. **92**, 4422 (2002)



$\text{Si}_{1-x}\text{Ge}_x$: Atomic Structure



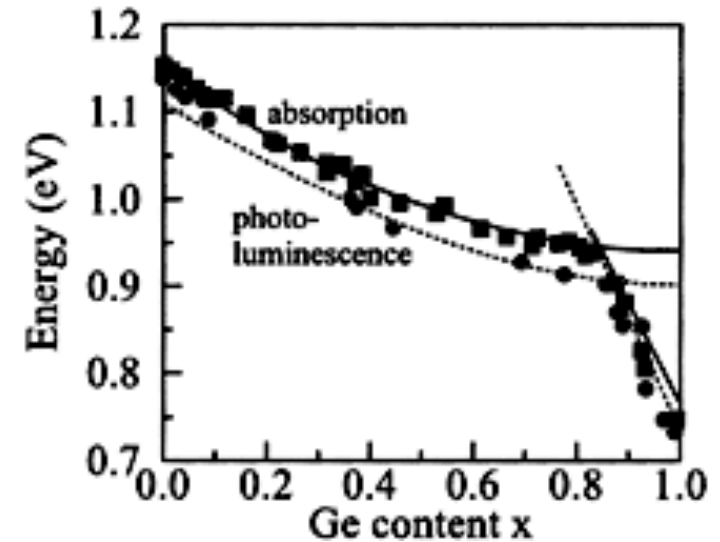
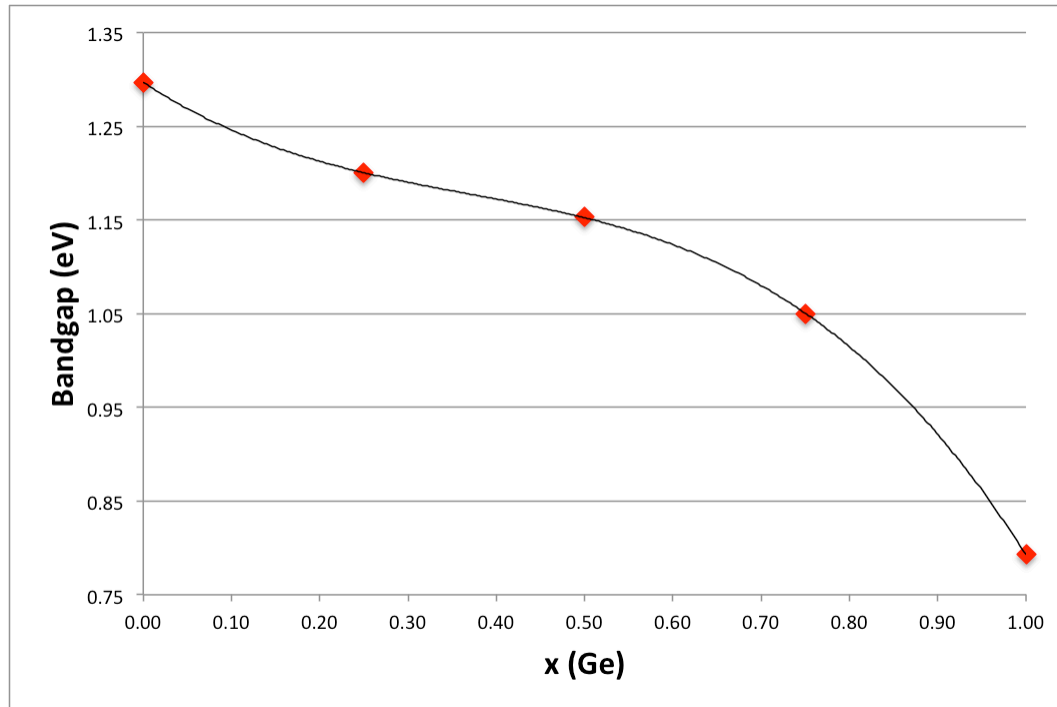
- $2 \times 2 \times 2$ supercell of diamond
- replace $x \times 64$ Si atoms by Ge
- cubic, space group P1
- relax structure



Computational parameters

- MedeA[®]-VASP 5.3
- PBEsol functional
- normal precision, real-space projection
- $\Delta \mathbf{k} \approx 0.2/\text{\AA}$, $3 \times 3 \times 3$ \mathbf{k} -points, Γ -centered

$\text{Si}_{1-x}\text{Ge}_x$: Electronic Structure



loff: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>

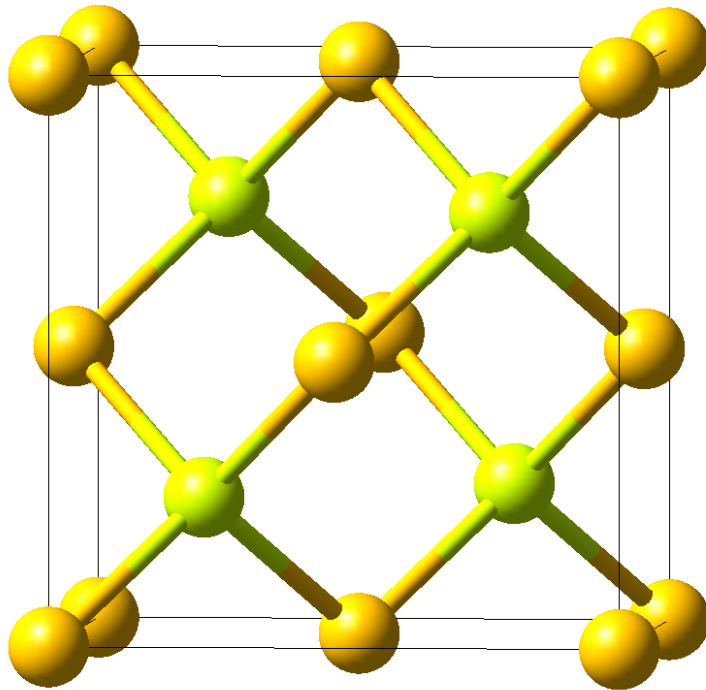
Computational parameters

- MedeA[®]-VASP 5.3
- mBJLDA functional
- normal precision, real-space projection
- $\Delta\mathbf{k} \approx 0.2/\text{\AA}$, $3 \times 3 \times 3$ \mathbf{k} -points, Γ -centered

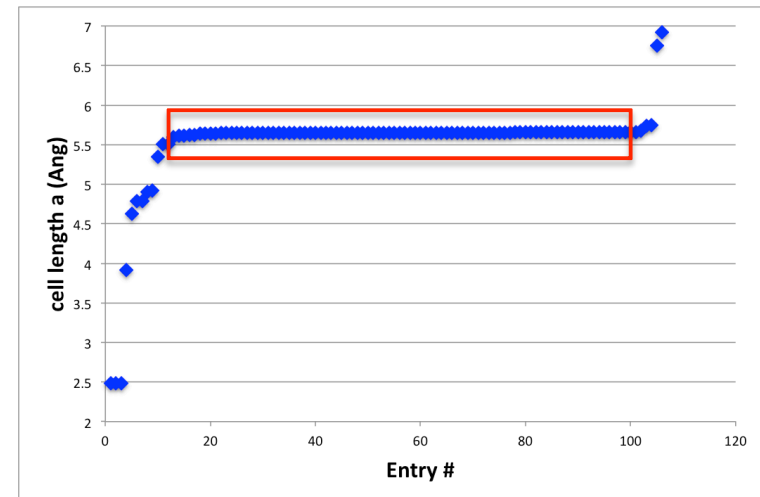
- calculations give band gap trend in close agreement with experimental data
- band gap variation due to disorder ≈ 0.05 eV
- band gap is slightly over-estimated



GaAs: Atomic Structure



- cubic, space group F-43m
- $a_{\text{comp}} = 5.671 \text{ \AA}$
- $a_{\text{exp}} \approx 5.65325 \text{ \AA}$ (Ioffe)
- $a_{\text{exp}} \approx 5.6477 \text{ \AA}$ (InfoMaticA *ave*)



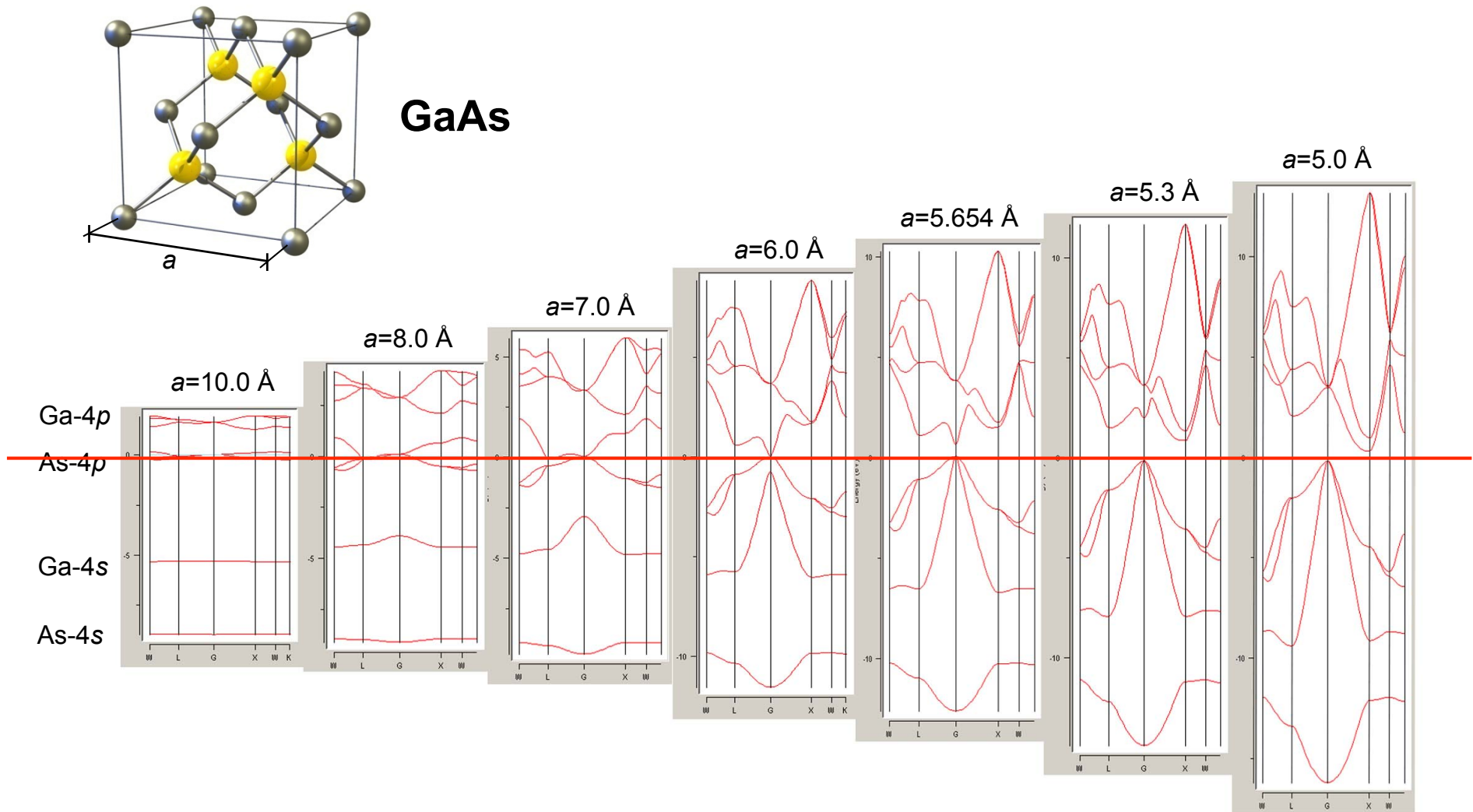
Ioffe: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>

Computational parameters:

- MedeA[®]-VASP 5.3
- PBEsol functional, spin-orbit relativistic
- standard 500 precision, reciprocal-space projection
- $\Delta \mathbf{k} \approx 0.2/\text{\AA}$, $11 \times 11 \times 11$ \mathbf{k} -points, Γ -centered

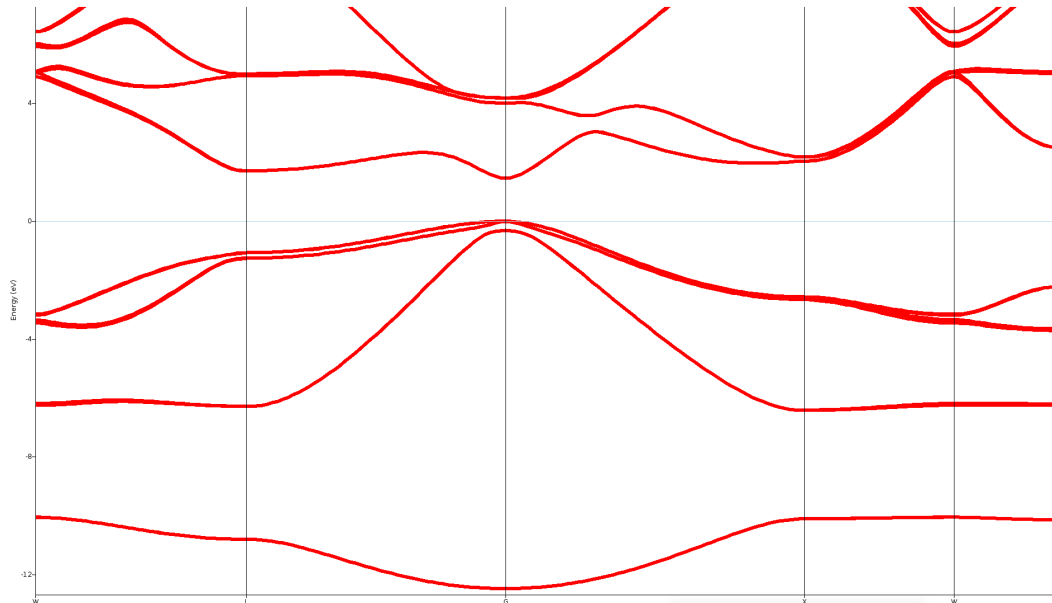


GaAs: Electronic Bands vs. Volume





GaAs: Electronic Structure



Source	a (Å)	Gap (eV)
mBJLDA	5.653	1.510
mBJLDA	5.671	1.472
loffe	5.653 (300K)	1.424 (300K)
loffe		1.519 (0K)
Handbook	5.653 (300K)	1.43 (300K)
Handbook		1.52 (0K)

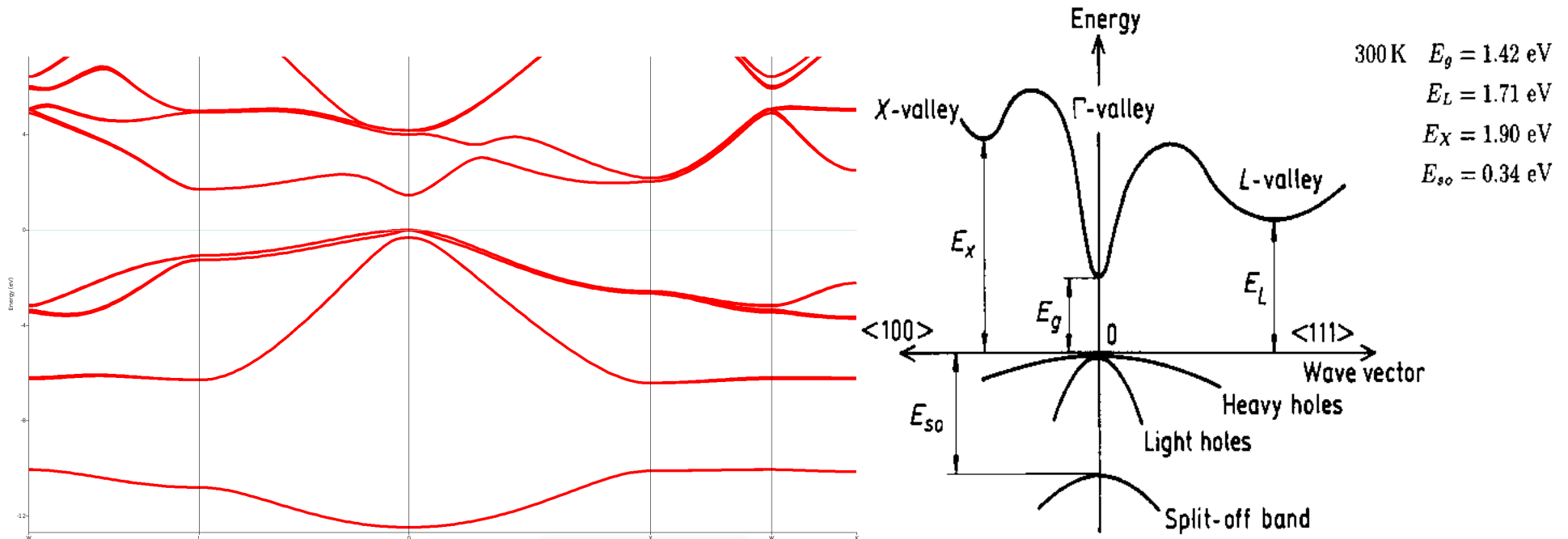
Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>
Handbook on Physical Properties of Semiconductors,
Vol. 2, ed. S. Adachi (Kluwer, Boston 2004)

Calculational Parameters

- MedeA[®]-VASP 5.3
- mBJLDA functional, spin-orbit relativistic
- normal precision, default plane-wave cutoff
- reciprocal-space projection, linear tetrahedron method
- $\Delta\mathbf{k} \approx 0.2/\text{\AA}$, $11 \times 11 \times 11$ \mathbf{k} -points, Γ -centered



GaAs: Electronic Structure



Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>
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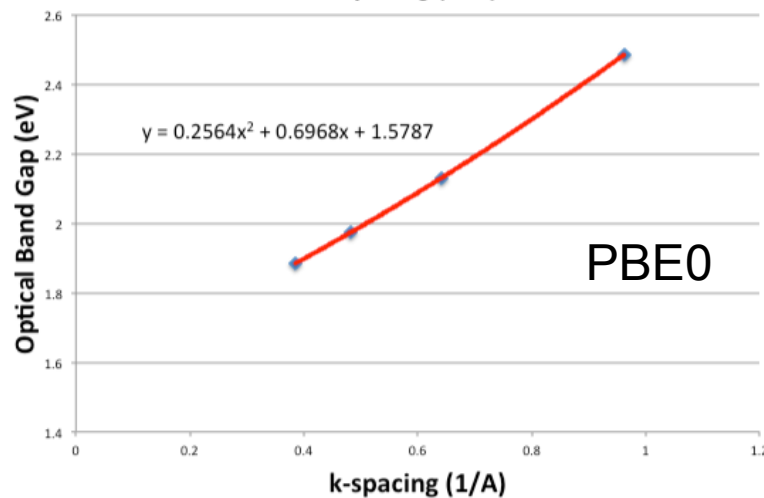
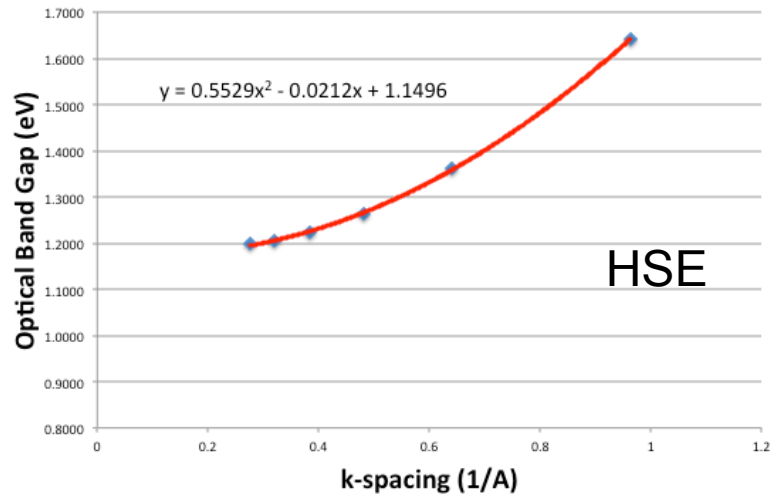
MedeA[®]-VASP

- computed band energies in good agreement with experimental data
- temperature effects (thermal expansion, phonons) may induce changes (≈ 0.1 eV)

	Exp. (0 K)	Exp. (300 K)	mBJLDA (5.653)	mBJLDA (5.671)
E_g	1.52	1.42	1.50	1.47
E_L	1.78	1.71	1.73	1.70
E_x	2.00	1.90	1.96	1.96
E_{so}	0.34	0.34	0.31	0.31



GaAs: Electronic Structure



- Γ -centered meshes
- identical for scf and nIX

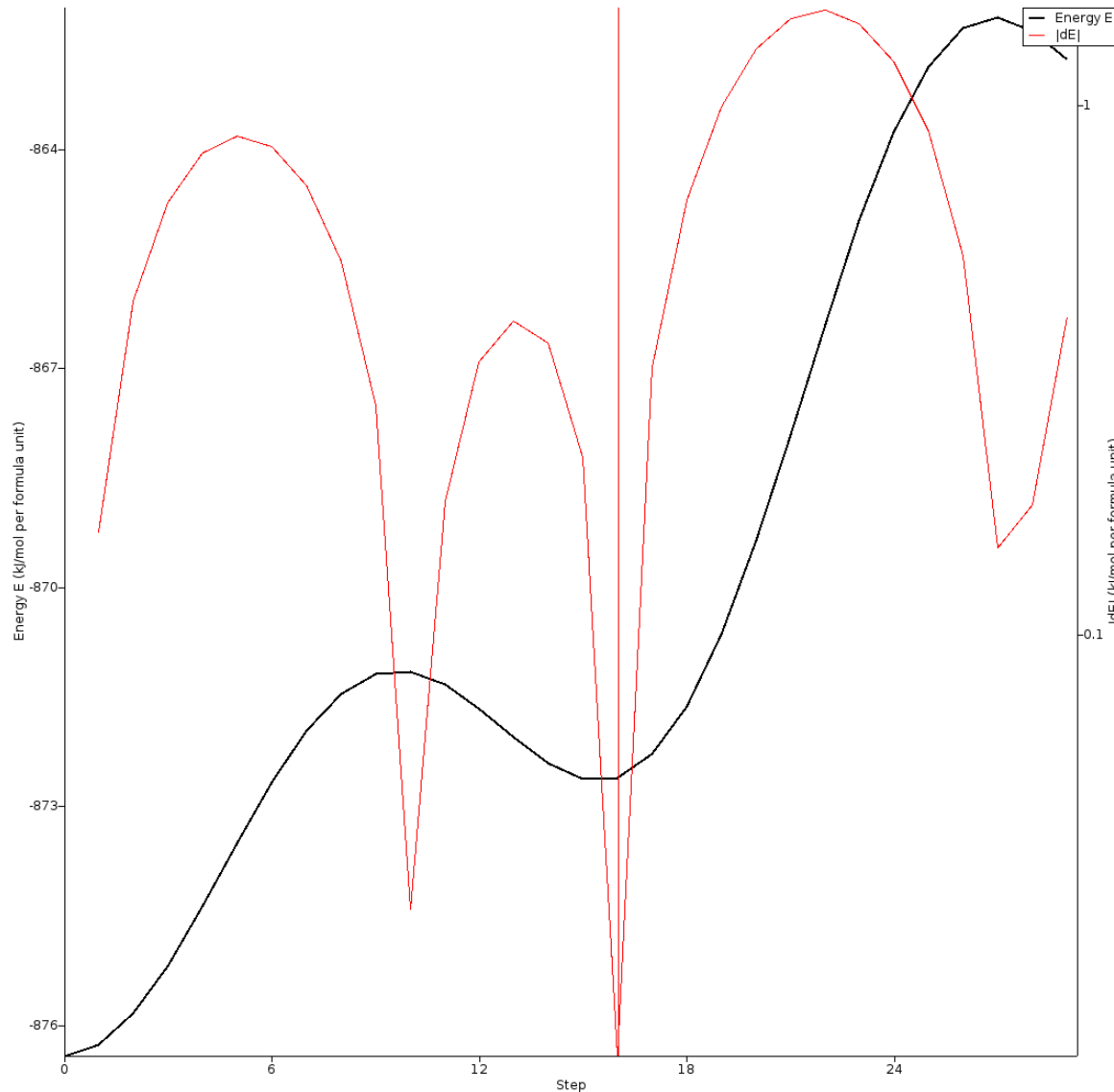
Source	a (Å)	Gap (eV)
HSE	5.655	1.15
PBE0	5.655	1.579
Ioffe	5.653 (300K)	1.424 (300K)
Ioffe		1.519 (0K)
Handbook	5.653 (300K)	1.43 (300K)
Handbook		1.52 (0K)

Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>
Handbook on Physical Properties of Semiconductors,
Vol. 2, ed. S. Adachi (Kluwer, Boston 2004)

- ▶ HSE underestimates E_{gap}
- ▶ E_{gap} depends on lattice constant!
- ▶ E_{gap} hardly depends on accuracy, pw-cutoff, # bands
- ▶ E_{gap} determined by smaller of scf and nIX k -spacing



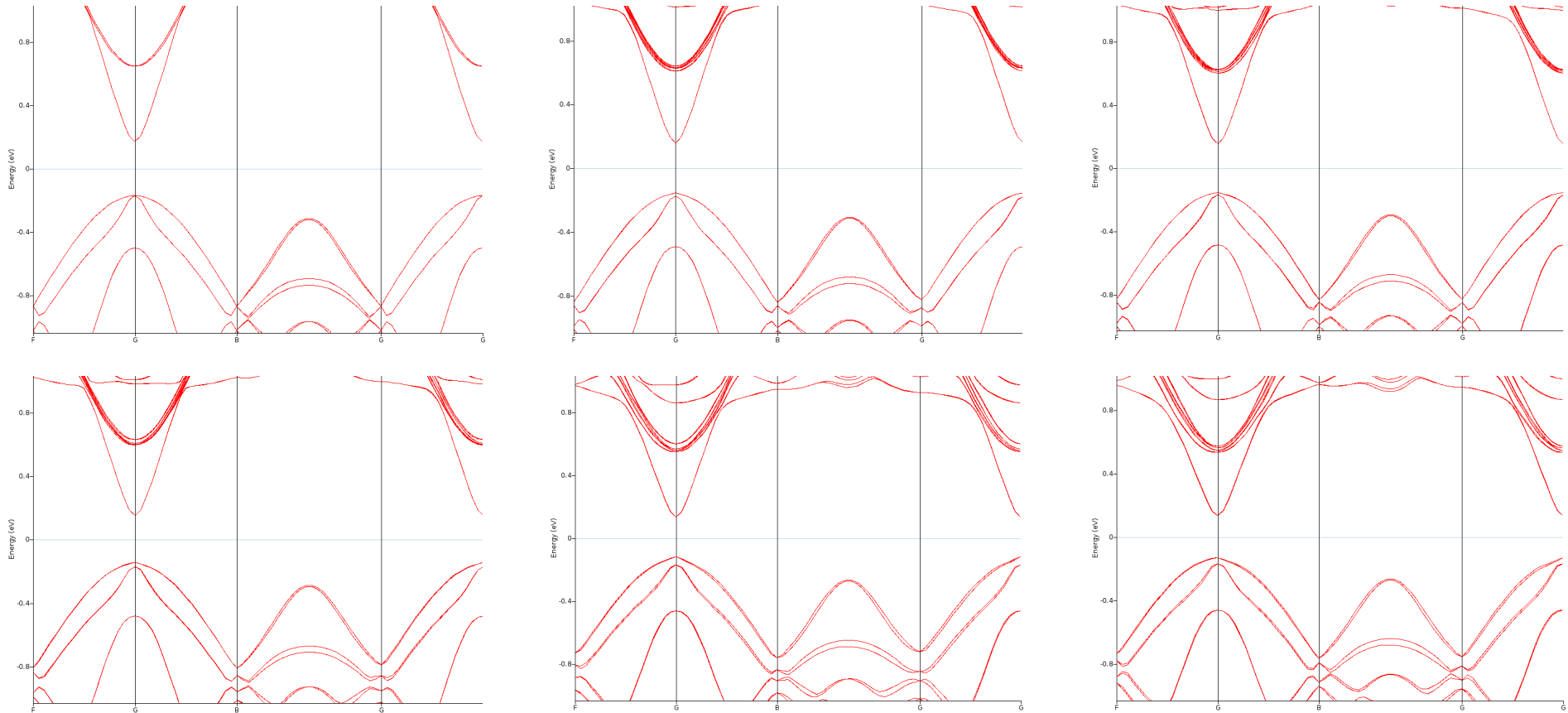
GaAs: MD Simulations



- ▶ Ab initio MD at 298 K
- ▶ 2×2×2 supercell
- ▶ MedeA[®]-VASP 5.3
- ▶ PBEsol functional
- ▶ SO coupling
- ▶ normal precision
- ▶ PW cutoff 282.691 eV
- ▶ real-space projection
- ▶ Γ -centered mesh with 0.3/Å **k**-point spacing, i.e. 2×2×2 **k**-points



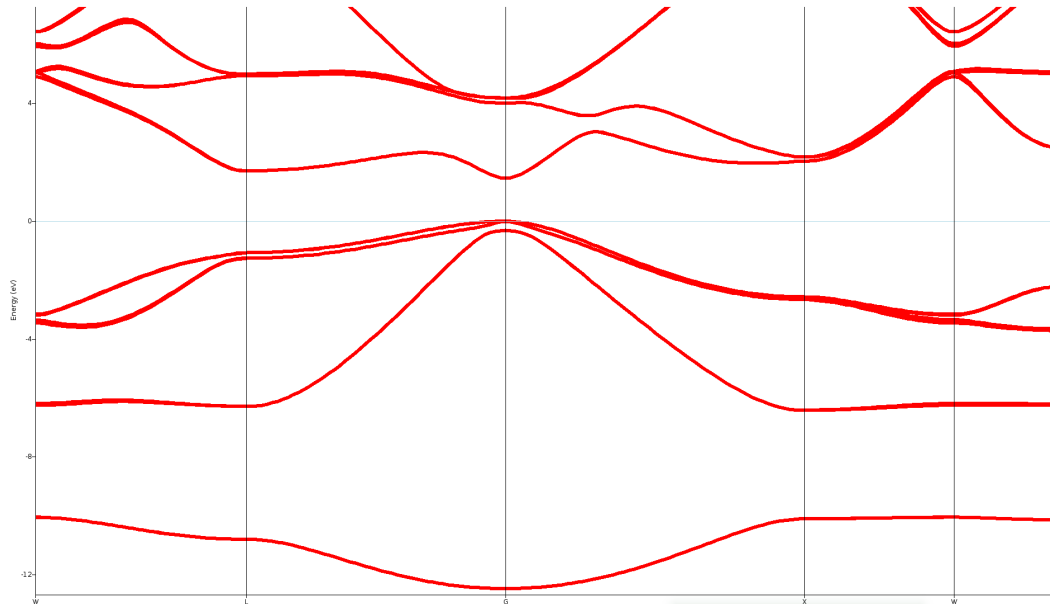
GaAs: MD Simulations



- ▶ band gap varies by ≈ 0.1 eV
- ▶ HH-LH and HH-SO splittings vary by ≈ 0.05 eV
- ▶ different splittings of 2nd conduction band



GaAs: Effective Masses



	Exp.	Exp.	MedeA
Electrons			
Eff. Mass @ Γ	0.063	0.064	0.088
Long. Eff. Mass @L	1.9	1.9	1.16
Trans. Eff. Mass @L	0.075	0.075	0.19
Long. Eff. Mass @X	1.9	1.3	1.01
Trans. Eff. Mass @x	0.19	0.23	0.20
Heavy Hole			
Eff. Mass	0.51	0.50	0.64/0.73
Light Hole			
Eff. Mass	0.082	0.082	0.098
Split-off band			
Eff. Mass	0.15	0.15-0.18	0.206

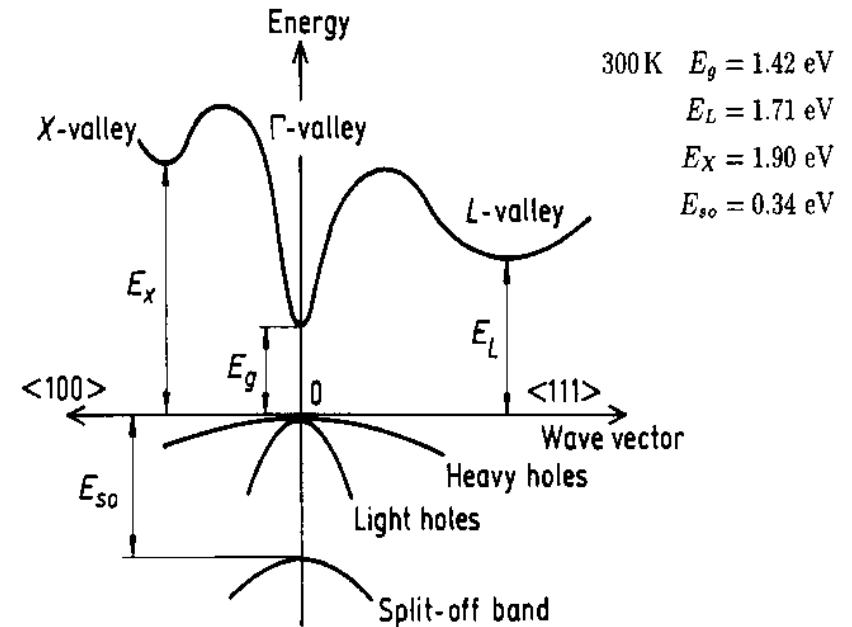
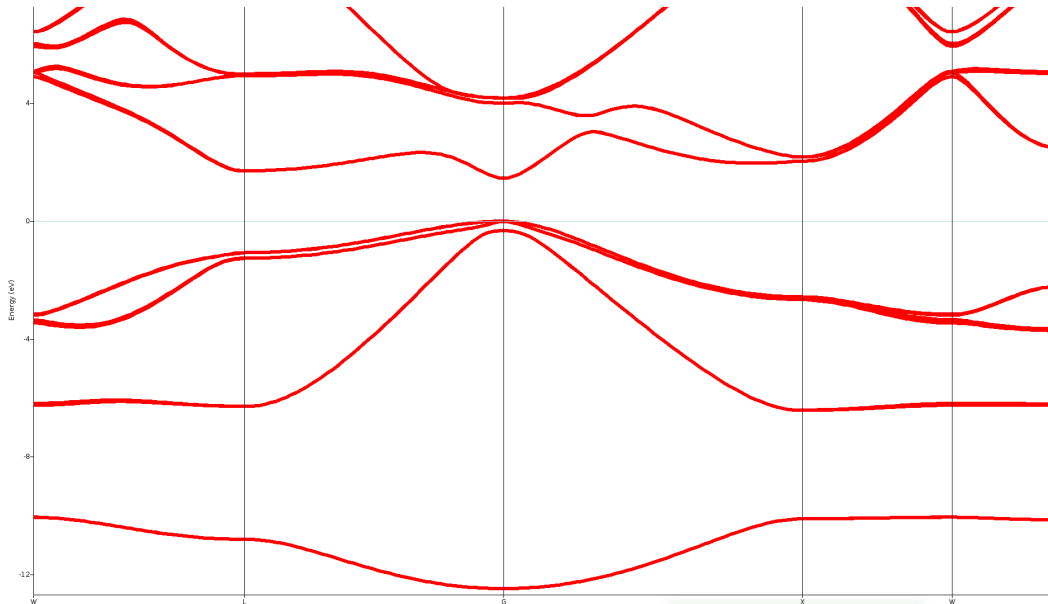
MedeA[®]-Electronics

- computed effective masses in good agreement with experimental data
- heavy hole mass beyond parabolic approximation

Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>
Handbook on Physical Properties of Semiconductors,
Vol. 2, ed. S. Adachi (Kluwer, Boston 2004)



GaAs: Effective Masses



Exp. data: <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/>
 Handbook on Physical Properties of Semiconductors,
 Vol. 2, ed. S. Adachi (Kluwer, Boston 2004)

MedeA[®]-Electronics

- directional effective masses in reasonable agreement with experimental data

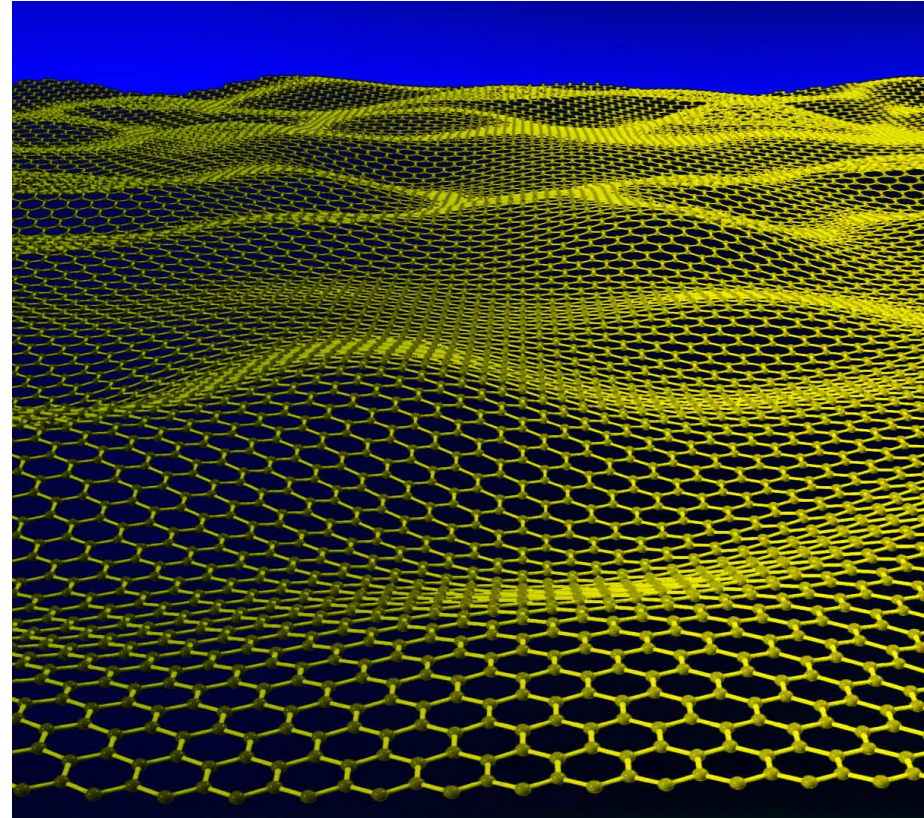
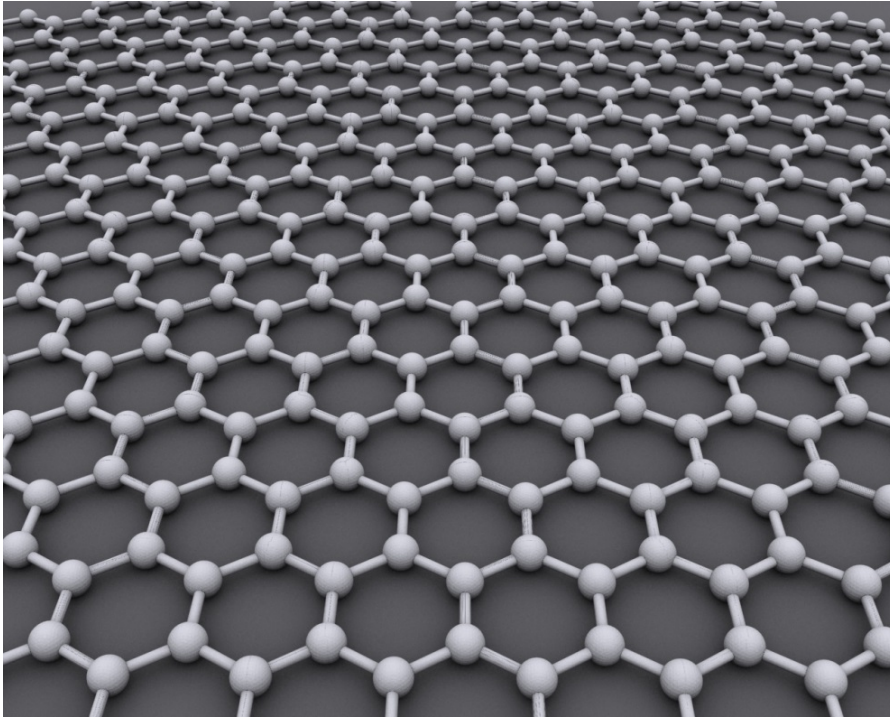
	Heavy Hole		Light Hole		Split-Off	
	Exp.	calc	Exp.	calc	Exp.	calc
<001>	0.330	0.314	0.090	0.099	0.154	0.207
<011>		2.949		0.089	-	0.208
<111>	0.780	2.838	0.077	0.084	0.178	0.205



Phonon Dispersions



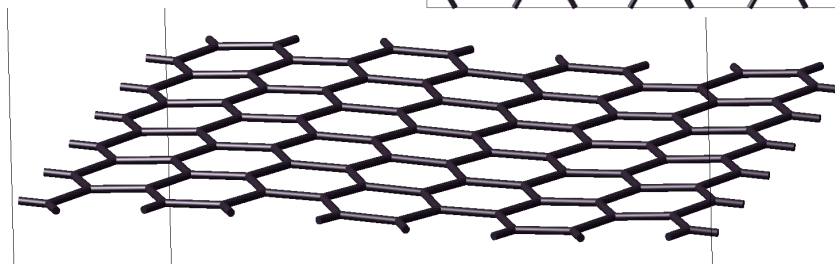
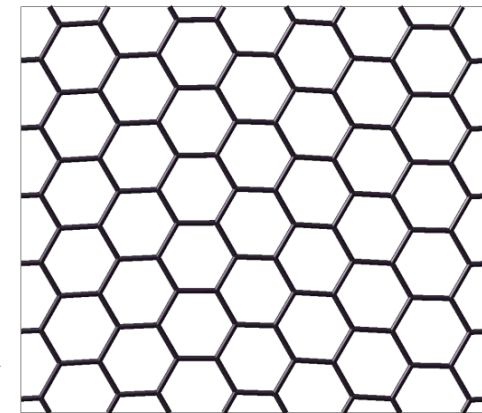
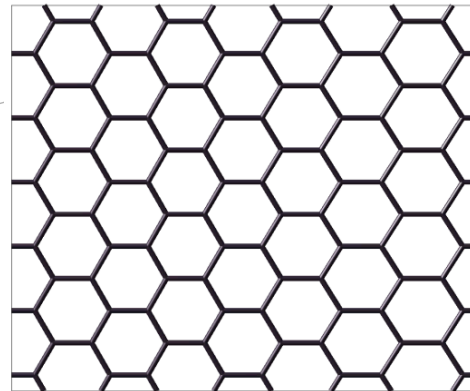
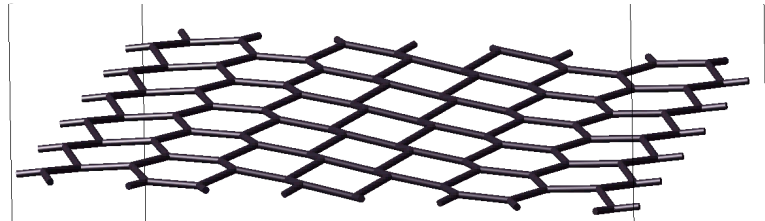
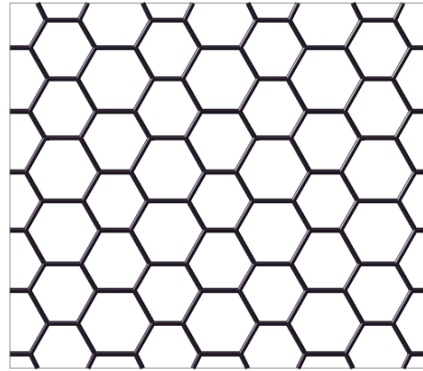
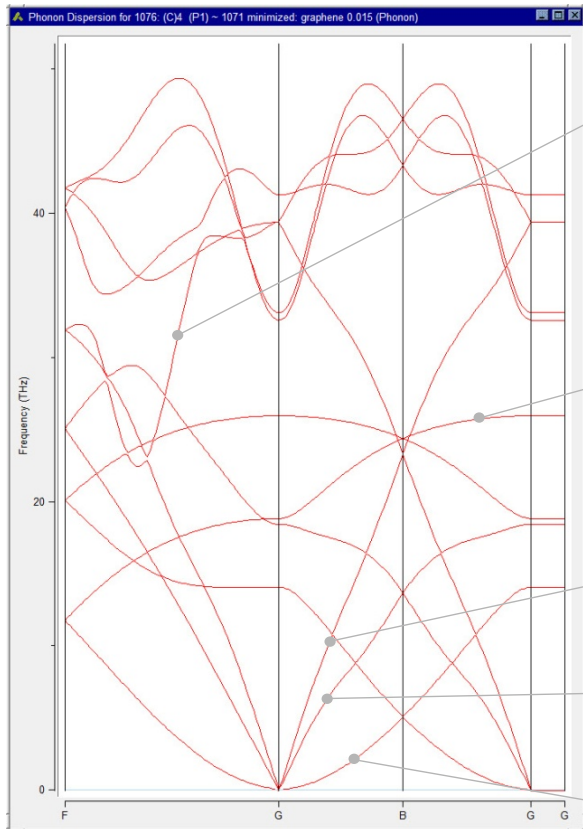
Graphene



- ▶ Konstantin Novoselov, Andre Geim
 - first isolated individual graphene planes in 2004
 - nobel prize 2010



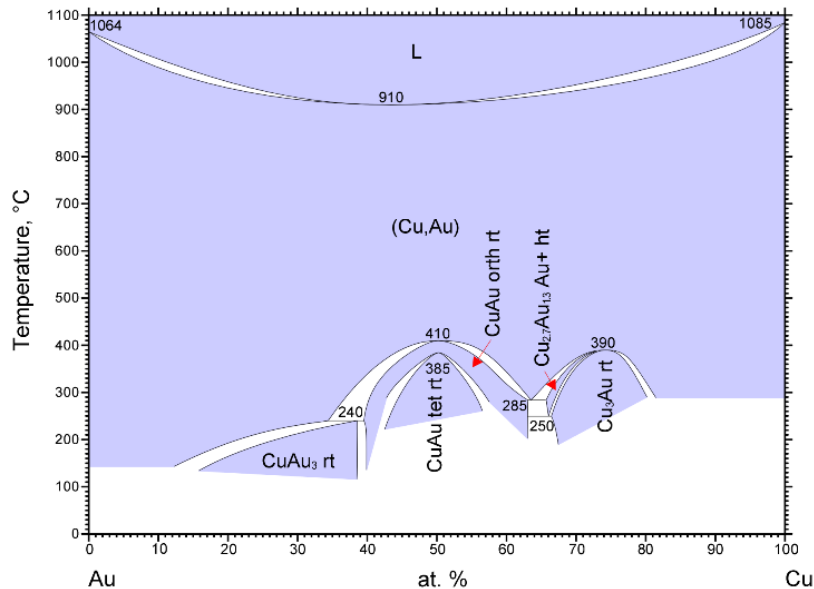
Analyze Phonons of Graphene





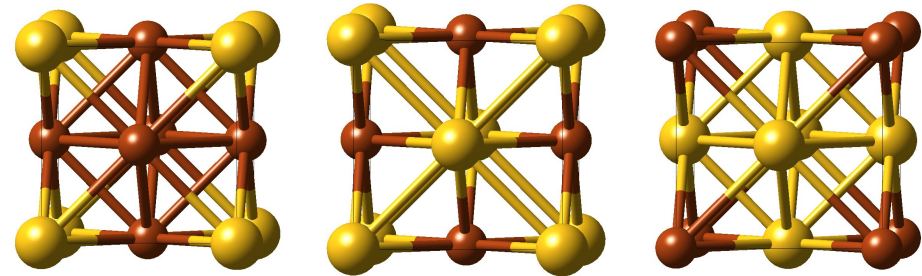
Electrical Conductivity in Disordered Materials

$\text{Cu}_{1-x}\text{Au}_x$: Intermetallic Phases

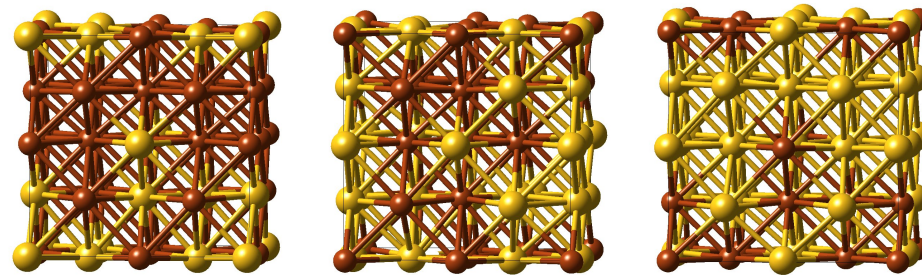


- wide range of solubility
- ordered and disordered phases

ordered cubic phases (InfoMaticA):



disordered cubic phases (SQS):



Cu_3Au

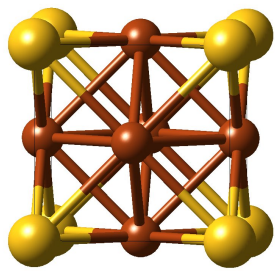
CuAu

CuAu_3

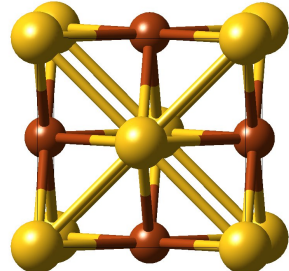
- ordered phases from literature (InfomaticA) and cluster expansion (CE)
- disordered phases modeled as quasi-random structure (SQS)
 - mimic first few correlation functions of perfectly random structures

$\text{Cu}_{1-x}\text{Au}_x$: Ordered Structures

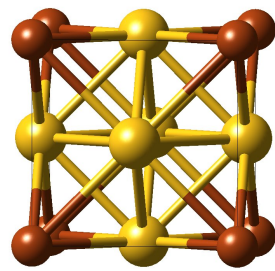
ordered cubic phases (InfoMaticA):



Cu_3Au

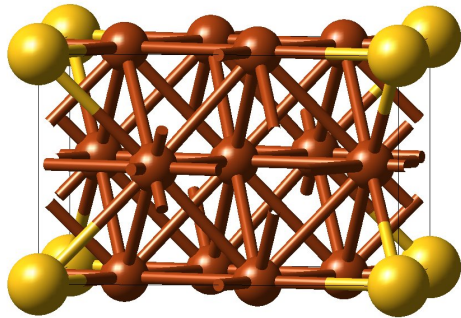


CuAu

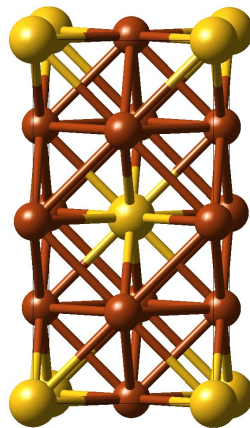


CuAu_3

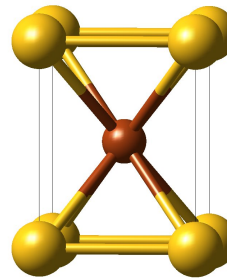
ordered tetragonal phases from cluster expansion (CE):



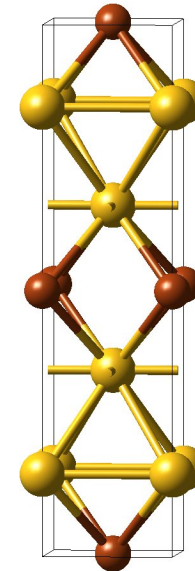
Cu_9Au



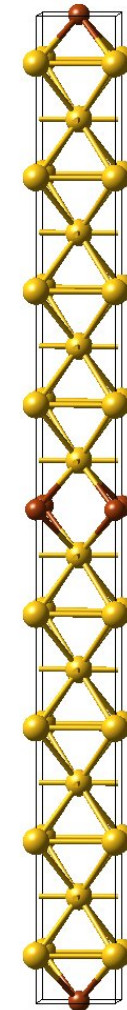
Cu_3Au



CuAu



CuAu_2

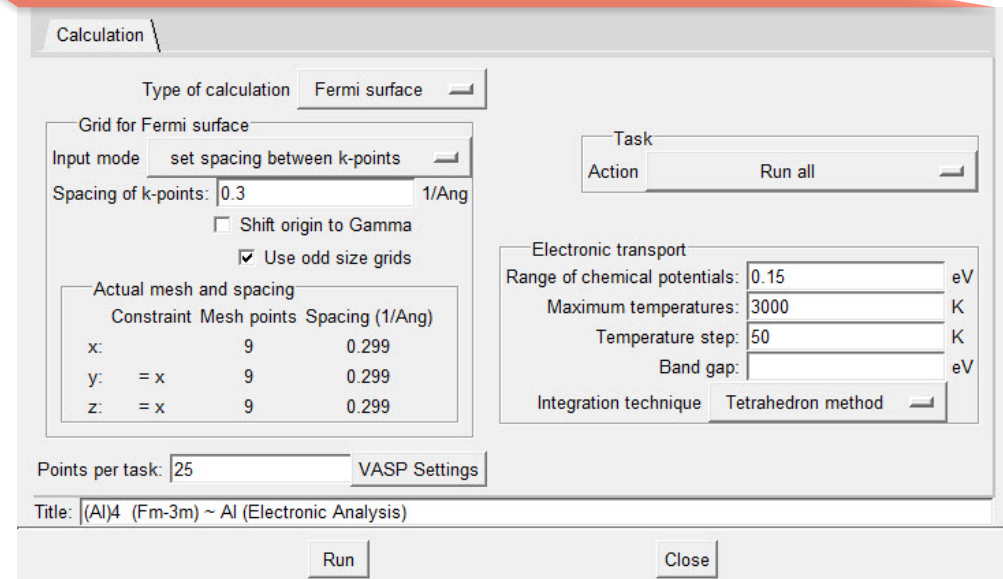


CuAu_8

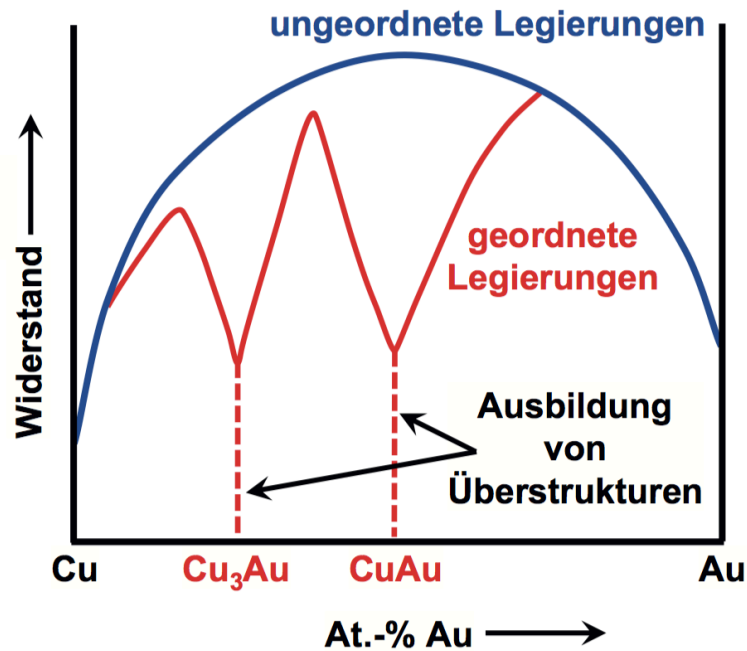


MedeA[®] Electronics

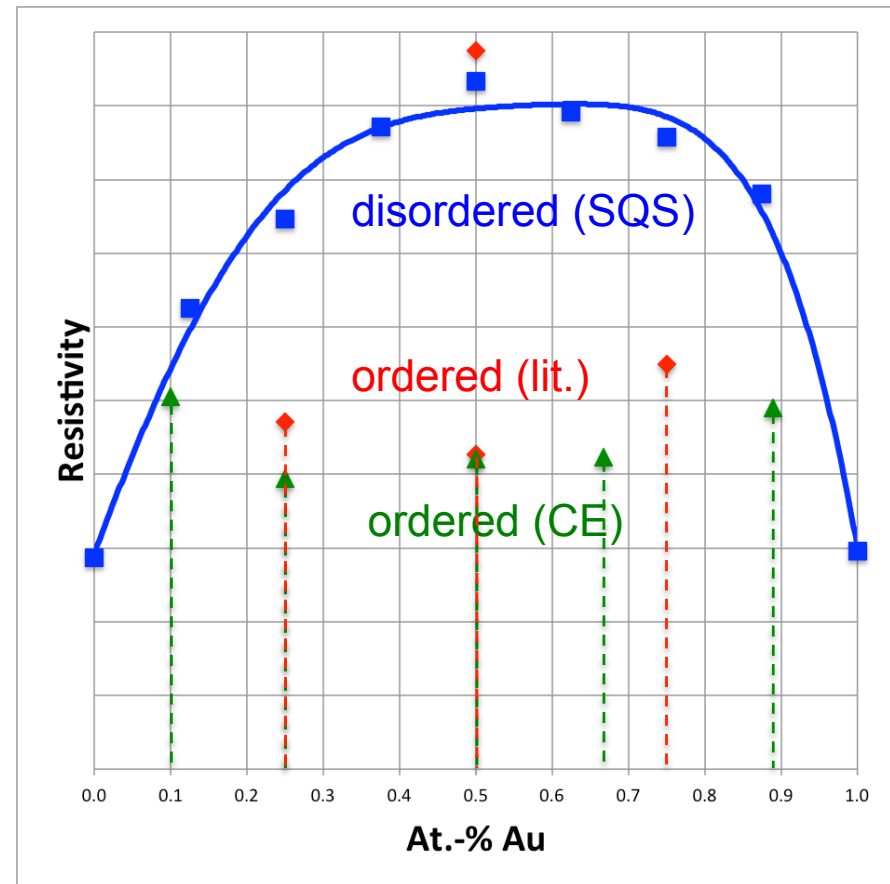
- ▶ Boltzmann theory: semiclassical theory
 - electrons follow classical equations of motion
 - electron velocity/effective mass from first principles
 - results depend on relaxation time (**critical!**)
- ▶ implemented in **MedeA[®] Electronics** (including BoltzTraP)
- ▶ calculated properties
 - electrical conductivity
 - thermopower (Seebeck coefficient)
 - thermal conductivity (electronic part)
 - electronic specific heat
 - Pauli paramagnetic susceptibility
 - Hall conductivity
- ▶ results vs. temperature or **doping**



Cu_{1-x}Au_x: Electrical Resistivities



Pecher, Haarmann, *Nachr. Chem.* **61**, 1017 (2013);
 Riedel, Janiak, *Anorg. Chem.* (de Gruyter, Berlin 2007)



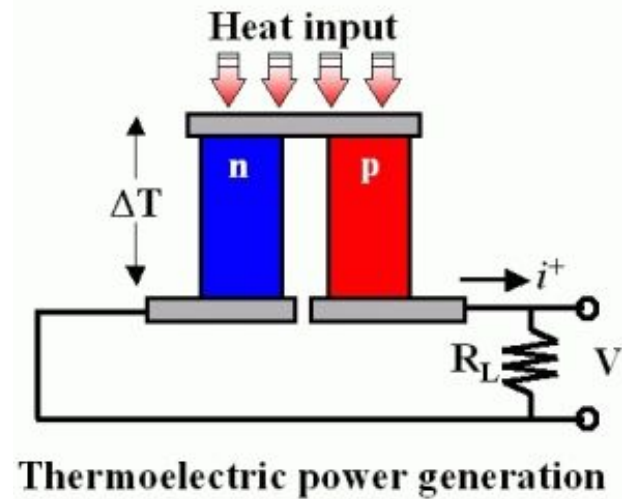
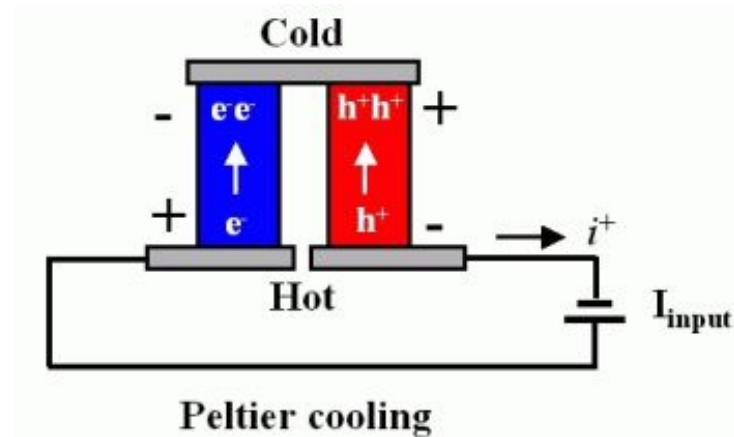
- ordered phases show systematically reduced electrical resistivities as compared to disordered alloys
- very good agreement of calculated data with experimental findings



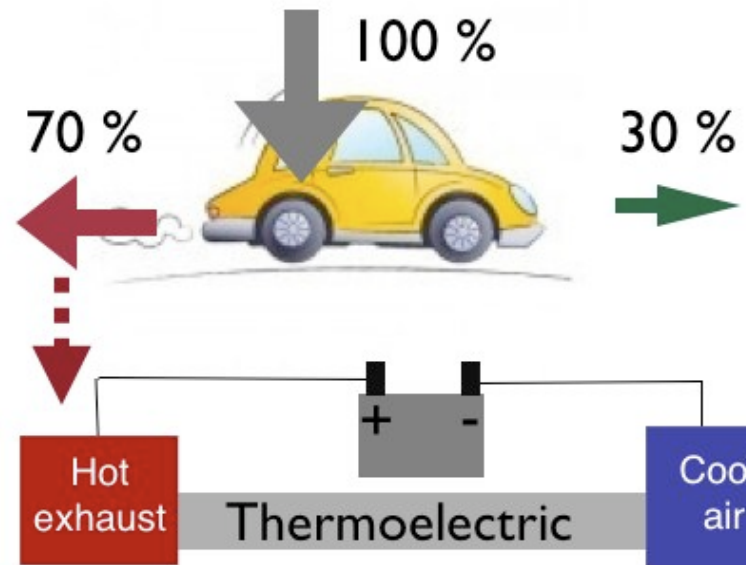
Thermoelectric Power of Bi_2Te_3



Thermoelectricity



- ▶ Peltier effect
 - use electric power for heating or cooling
- ▶ Seebeck effect
 - convert heat into electric power





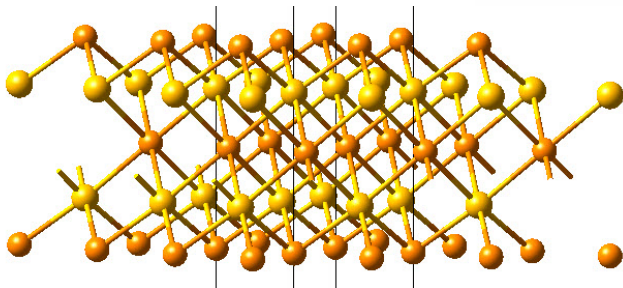
Promising Candidates

Figure of merit:

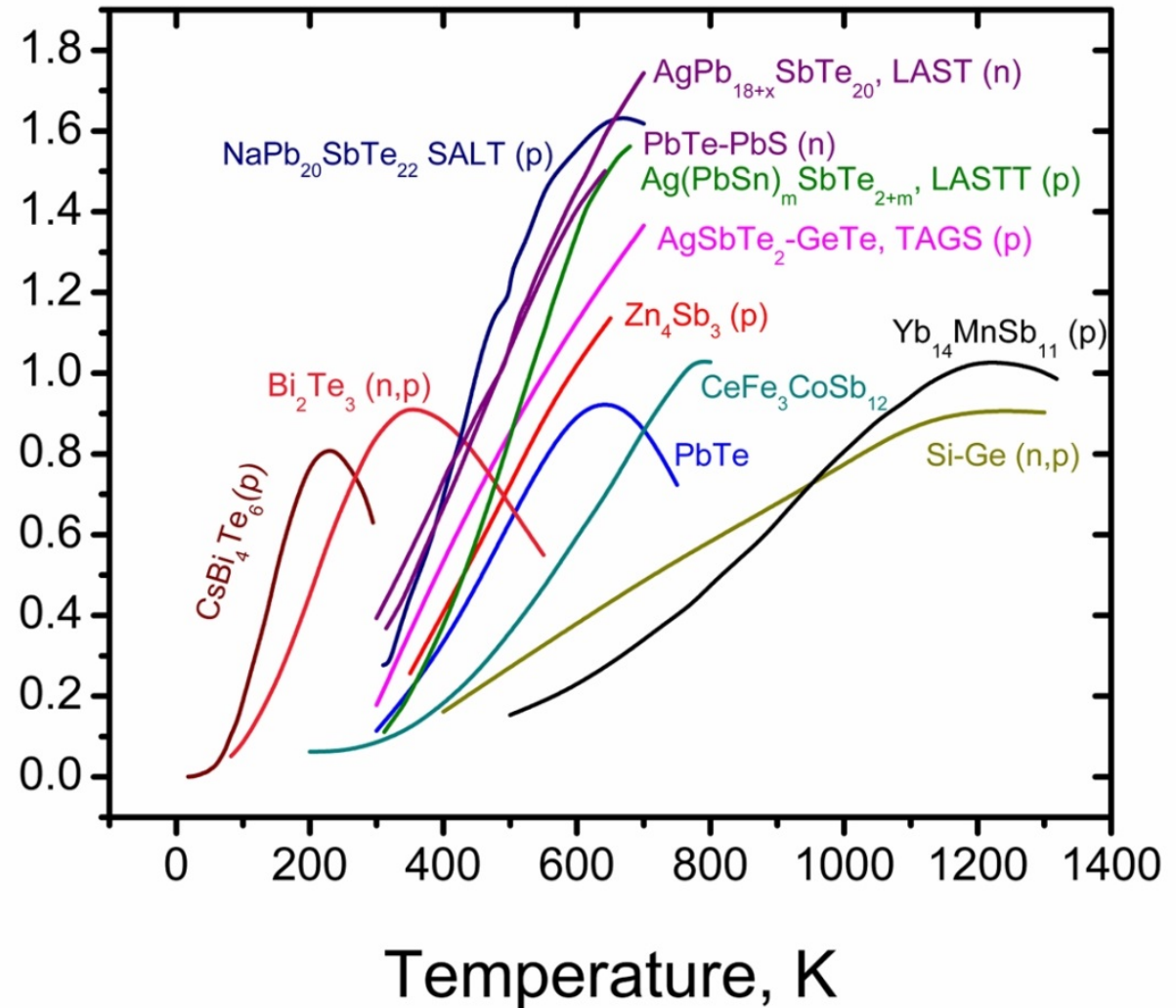
$$Z = \sigma S^2 / \kappa$$



- ▶ layered structure
- ▶ narrow-gap semiconductor
- ▶ efficient thermoelectric when doped with Sb or Se



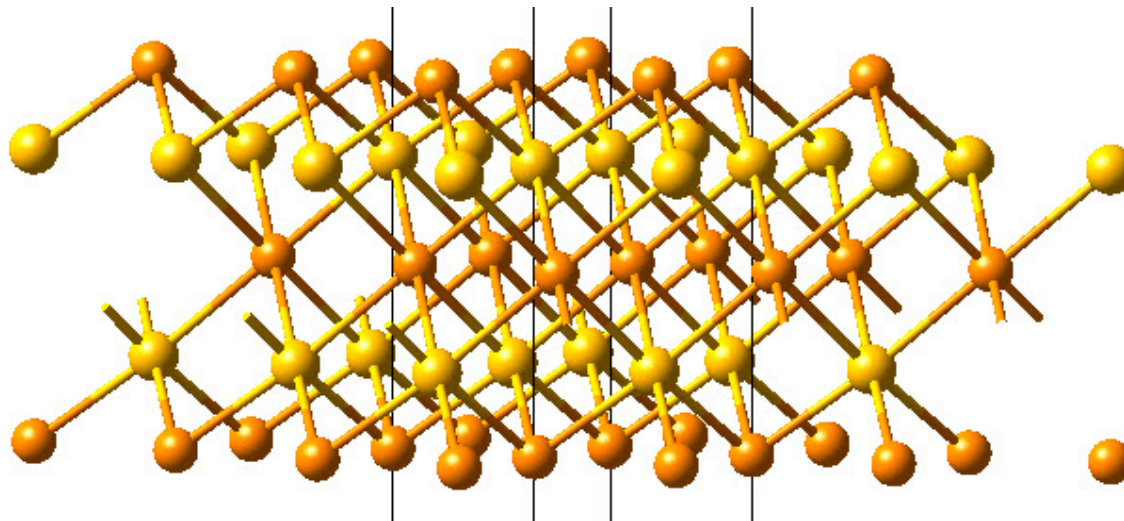
ZT





Retrieve structure of Bi_2Te_3

- ▶ **Tools** → **InfoMaticA**, **InfoMaticA** → **Search**, **Clear**
- ▶ Define the search criteria
 - **Formula is Bi_2Te_3**
 - **Structural completeness is *Complete***
- ▶ Retrieve the relevant crystal structures of Bi_2Te_3
 - Select structures *ICSD.42546* (hexagonal setting of rhombohedral phase)
 - **Right-click** on one selected record → **View**
 - Draw bonds: **Right-click** in the structure window → **Edit bonds...**, **OK**



layered rhombohedral structure

- ▶ covalent bonding within slabs
- ▶ van der Waals bonding between slabs

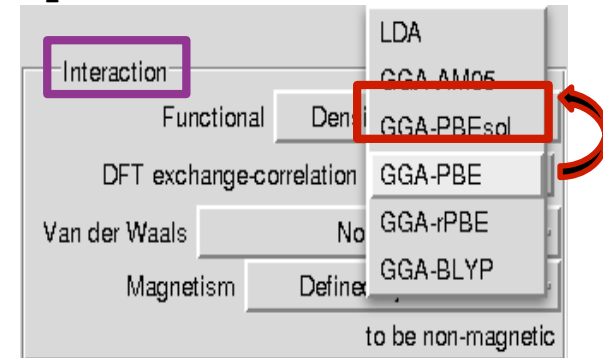
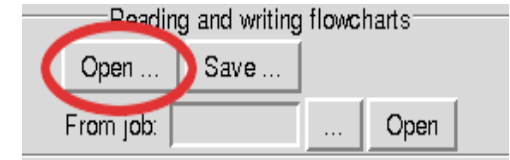


Optimize Structure

▶ Activate Bi₂Te₃ structure

▶ **Job Control** → **New Job...**

- **Right-click** on left area → **Clear**
- **Open ...** → Load the flowchart `Bi2Te3-full-optimization.flow` from the training flowchart folder
- **Right-click** on VASP stage → **Edit...**
- Change DFT exchange-correlation to **GGA-PBEsol**
- **Ok**
- Enter as **Job title:**
`Bi2Te3 full optimization PBEsol+SOI`
- **Run**

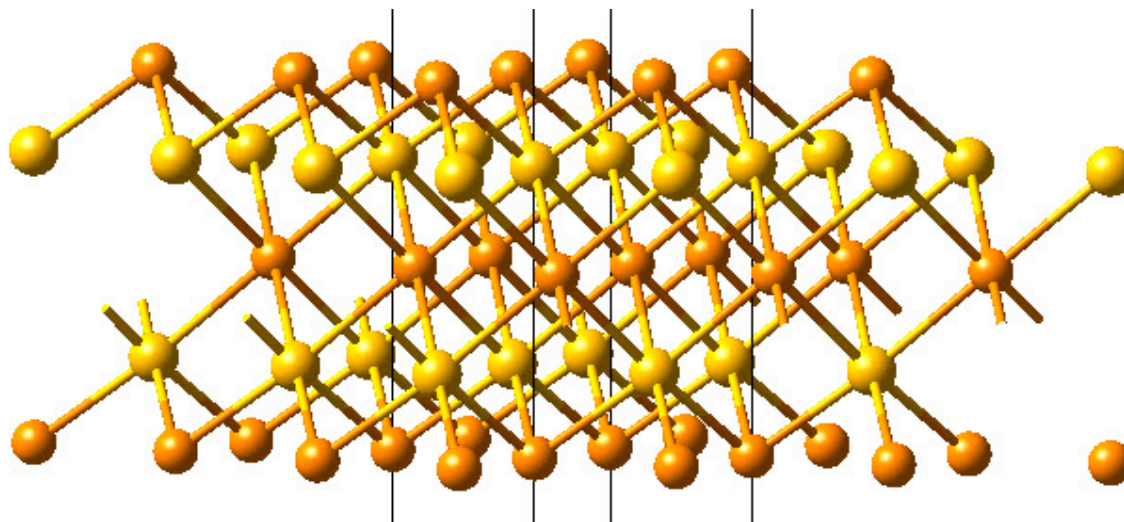


(Only set up the VASP jobs but do not actually run them!)



Monitor and load optimized structure

- ▶ Clear MedeA® workbench: **Windows** → **Close all windows**
- ▶ Check and analyse results:
 - **Job Control** → **View and Control Jobs** (opens JobServer interface in web browser)
 - Click on **Jobs** and afterwards on relevant job number of the running jobs
 - Check the progress of the calculation (indicated by **Available Results**)
- ▶ Upon completion of jobs load the optimized structures
 - **File** → **Open...** → **Previous Calculation**
 - Select the `final`: record of the relevant job
 - **Insert >>, Ok**



layered rhombohedral structure

- ▶ covalent bonding within slabs
- ▶ van der Waals bonding between slabs



Set up MedeA[®] Electronics job

- ▶ Activate the optimized tetragonal structure
- ▶ Open Electronics module: **Tools** → **Electronics**, **Electronics** → **Run**

Calculation

Type of calculation: Fermi surface

Grid for Fermi surface

Input mode: set spacing between k-points

Spacing of k-points: 0.1 1/Ang

Shift origin to Gamma

Use odd size grids

Actual mesh and spacing		
Constraint	Mesh points	Spacing (1/Ang)
x:	17	0.098
y: = x	17	0.098
z: = x	17	0.098

Points per task: 25

VASP Settings

Task: Run all

Electronic transport

Range of chemical potentials: 2.0 eV

Maximum temperature: 3000 K

Temperature step: 50 K

Band gap: eV

Integration technique: Tetrahedron method

Title: (Bi2 Te3)3 (R-3MH setting of R-3m) ~ Bi2Te3_DC16427_min (Electronics)

Run Close

- Spacing of k-points: **0.1** 1/Ang
- select **VASP settings**



Submit MedeA[®] Electronics job

- ▶ In VASP GUI
 - **Restore defaults**
 - Calculation type: **Single Point** (Calculation panel)
 - DFT exchange-correlation: **GGA-PBESol** (Calculation panel)
 - Magnetism: **Spin-orbit magnetic** (Calculation panel)
 - Spacing of k-points: **0.2** 1/Ang (SCF panel)
 - **OK**

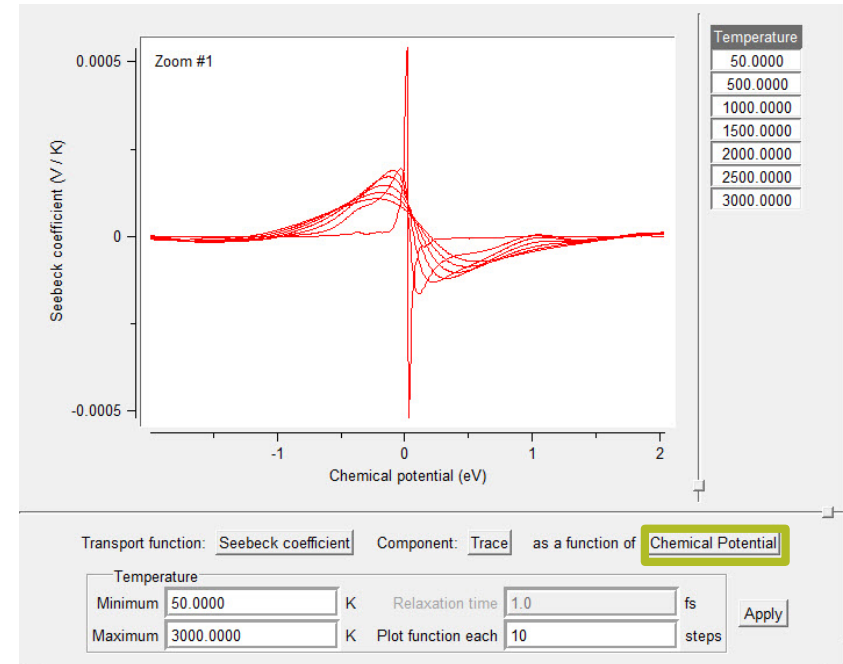
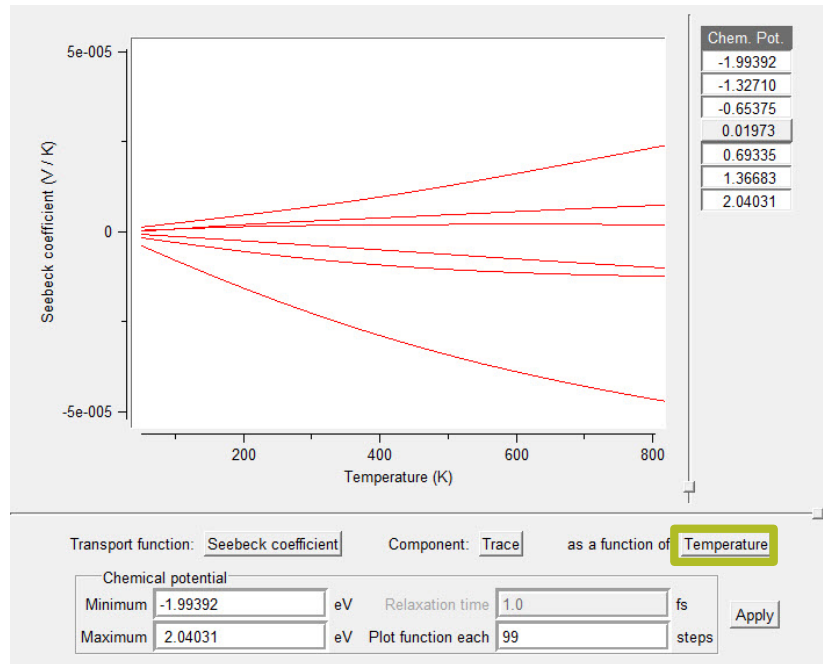
- ▶ Back in Electronics GUI
 - Enter **Title:** *(Bi₂Te₃)₃ (R-3MH setting of R-3m) (Electronics)*
 - **Run (Only set up the VASP jobs but do not actually run them!)**

- ▶ Check and analyse results:
 - **Job Control** → **View and Control Jobs** (opens JobServer interface in web browser)
 - Click on [Jobs](#) and afterwards on relevant job number of the running jobs
 - Check the progress of the calculation (indicated by **Available Results**)

- ▶ Display electronic transport properties
 - **Electronics** → **Electronic Transport**
 - Select record of the relevant job
 - **Insert >>, Ok**



Analyze results for Bi_2Te_3

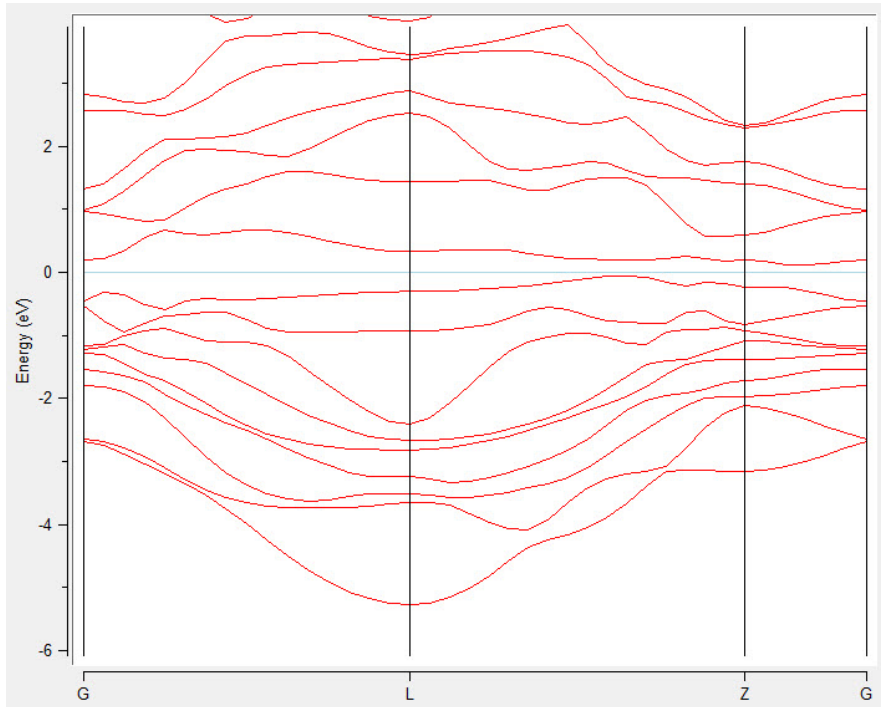


- ▶ display results as a function of
 - *Temperature*
 - *Chemical Potential*
- ▶ select/unselect single curves

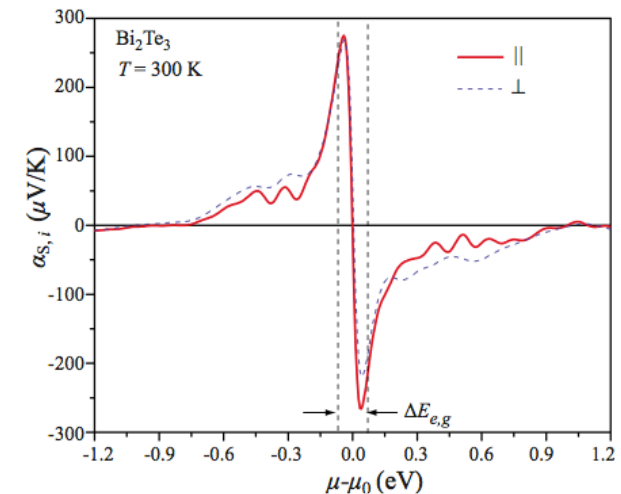
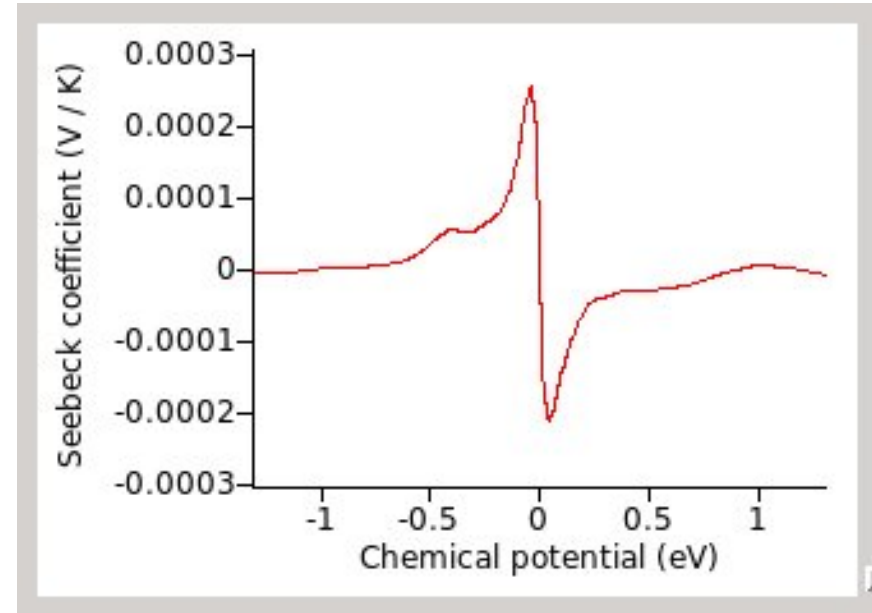
- ▶ thermoelectric power depends
 - strongly non-linear on doping
 - almost linear on temperature



MedeA[®] Electronics: Bi₂Te₃

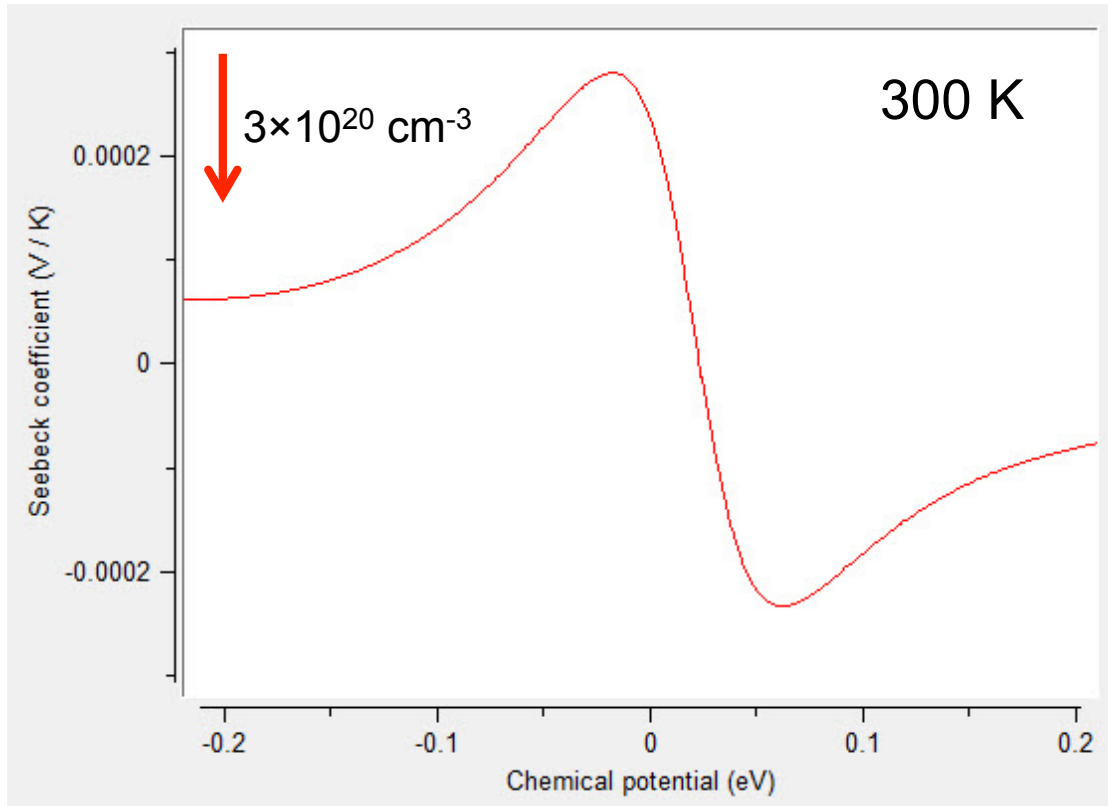


- ▶ indirect band gap, $E_g=0.16\text{eV}$
- ▶ experiment: $E_g\approx 0.18\text{eV}$
(Sehr, Testardi, JPCS 1962)





MedeA[®] Electronics: Bi₂Te₃



► calculated Seebeck coefficient

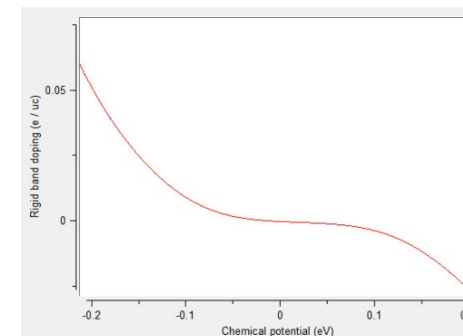
- $S \approx 300 \text{ } \mu\text{V/K}$ for p-type doping
- $S \approx 220 \text{ } \mu\text{V/K}$ for n-type doping

► experiments (RT)

- $S \approx 260 \text{ } \mu\text{V/K}$ at $4 \times 10^{18} \text{ cm}^{-3}$ p-type
- $S \approx 250 \text{ } \mu\text{V/K}$ at $7.4 \times 10^{18} \text{ cm}^{-3}$ n-type
- $S \approx 287 \text{ } \mu\text{V/K}$ n-type

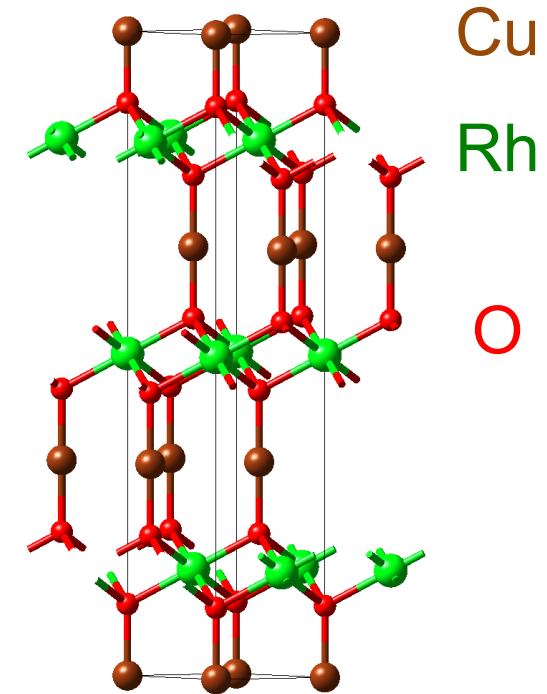
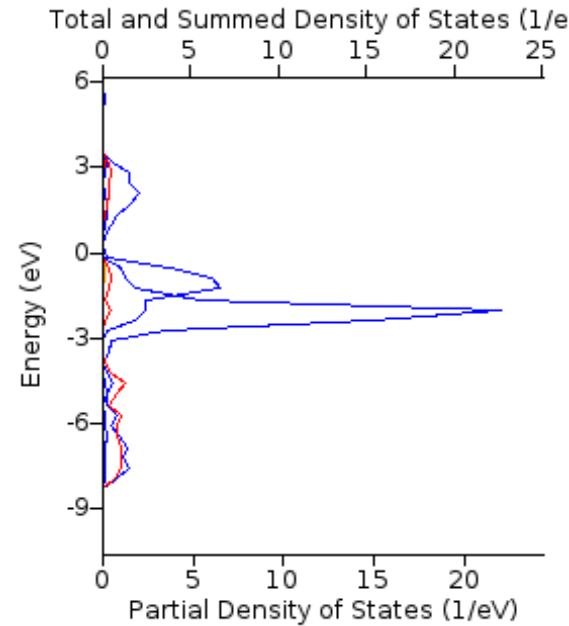
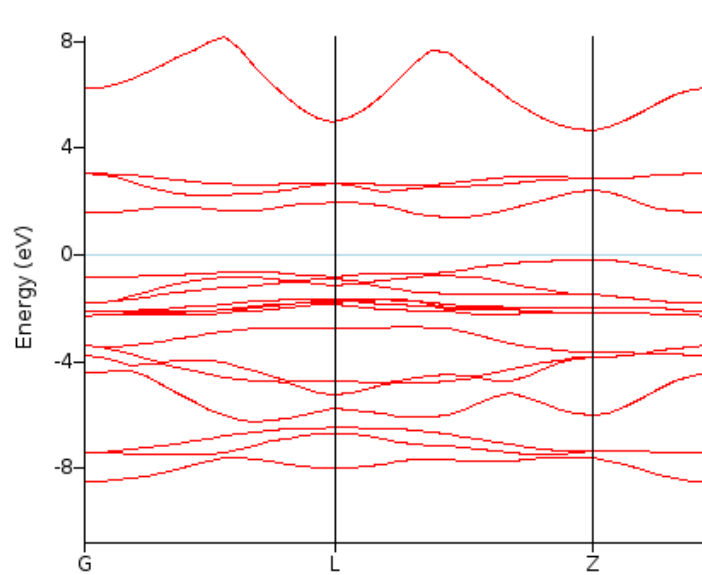
H.J.Goldsmid, Thermoelectric Refrigeration (NY, Plenum 1964)

J. Tan, Proc. SPIE 5836 (2005)

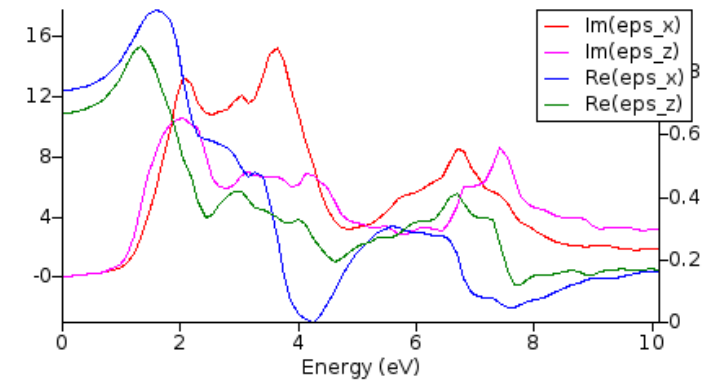




CuRhO₂: Thermopower

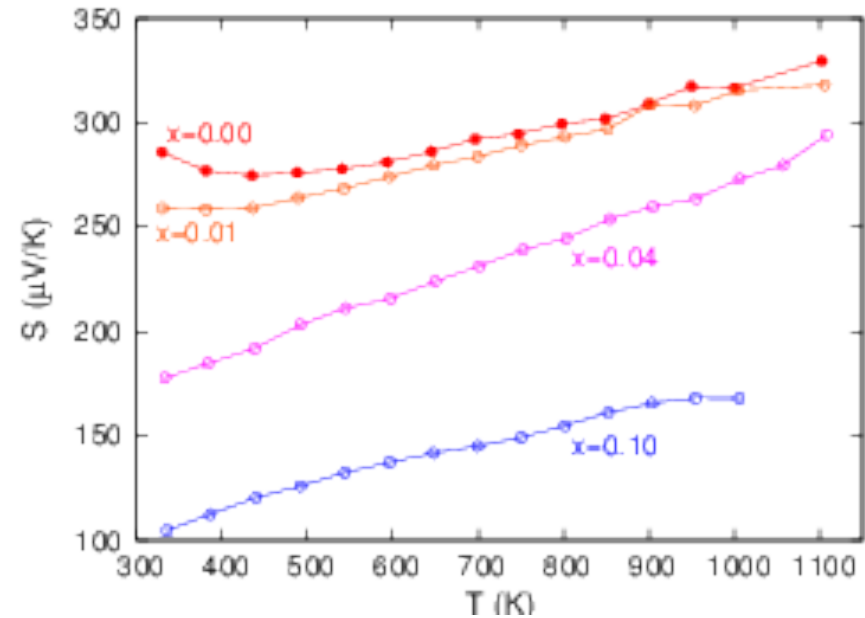
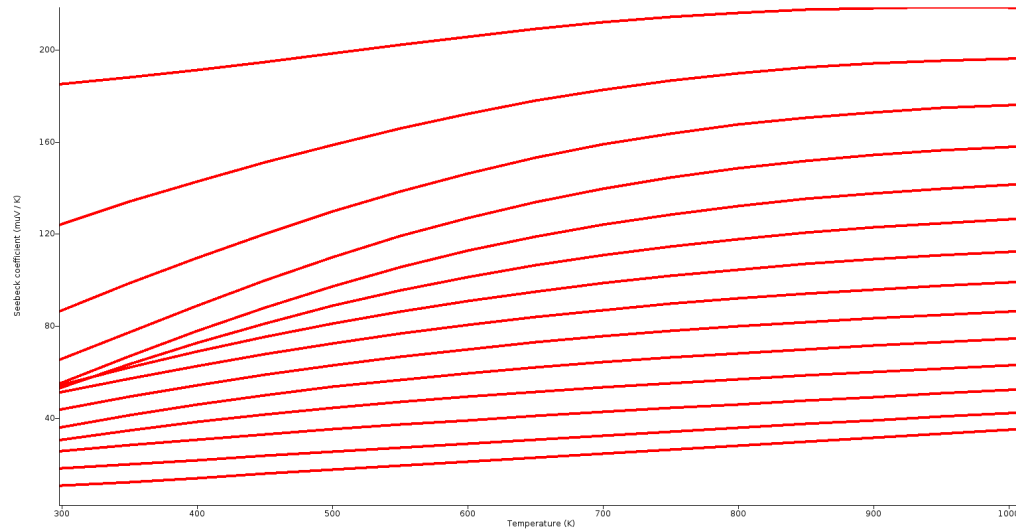


- ▶ delafossite structure
 - rhombohedral lattice
 - RhO₂ sandwiches (t_{2g}/e_g -splitting)
 - linear O-Cu-O bonds (sharp DOS-peaks)
- ▶ semiconductor
- ▶ CuRh_{1-x}Mg_xO₂: thermoelectricity





CuRhO₂: Thermopower



experimental data: A. Maignan, VE, C. Martin, S. Kremer, R. Frésard, D. Pelloquin, PRB **80**, 115103 (2009)

► good qualitative agreement

- positive thermopower for hole doping ($0 < x < 10^{22}$ el/cm³)
- positive slope up to about 1000 K

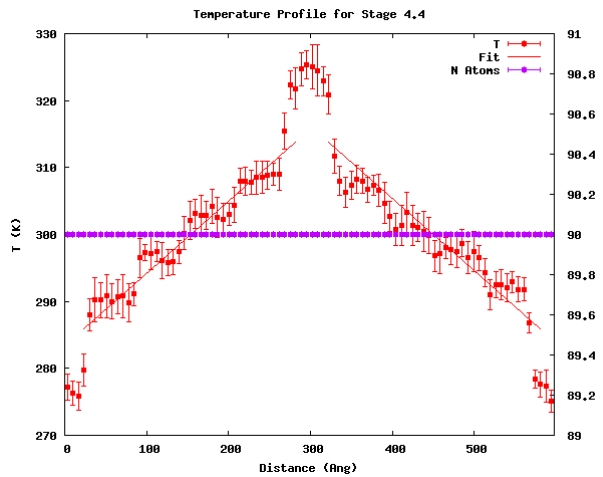
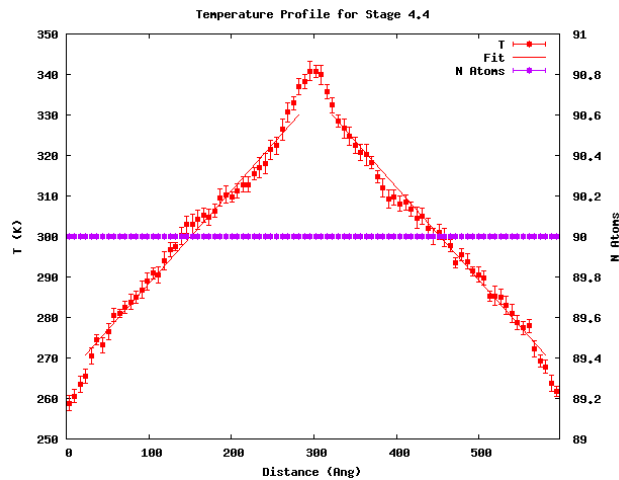


Thermal Conductivity



Si-Ge Alloys: Thermal Conductivity

- ▶ Reducing the lattice thermal conductivity enhances ZT
- ▶ Improved understanding of the effect of composition and processing on thermal conductivity allows to tailor materials on the atomic scale

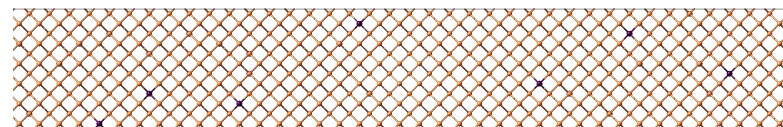


κ at 300 K in W/(m·K)

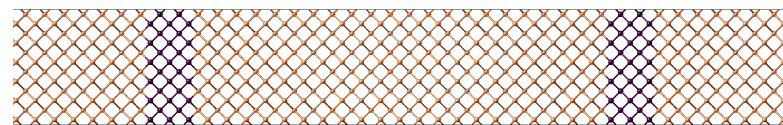
Sys.	Calc.	Expt(*)
Si	128	130
Ge	37	58

* Data from Ioffe Institute

System	Alloy	λ (Wm ⁻¹ K ⁻¹)
Si ₄₃ Ge	random	6.87
Si ₄₃ Ge	layered	3.71
Si ₄₃ Ge ₅	layered	1.87



random Si_xGe_{1-x}

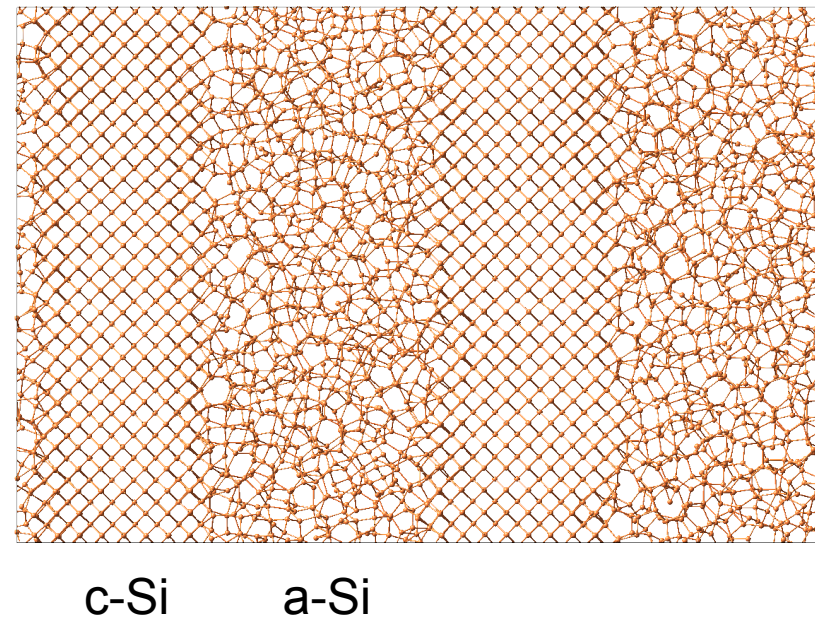
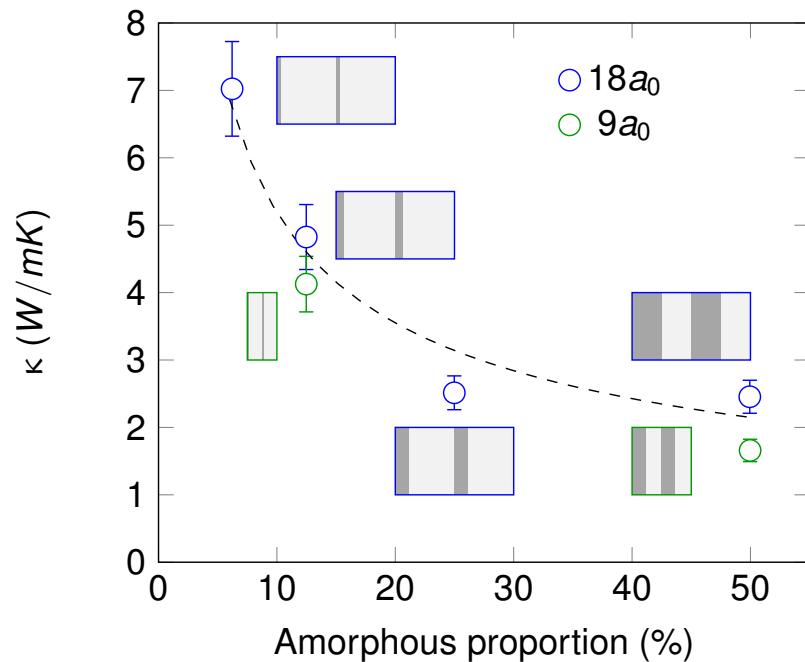


layered Si_xGe_{1-x}



a-Si/c-Si: Thermal Conductivity

- ▶ Introducing disorder can drastically reduce κ , and increase ZT
- ▶ This can be done without changing the composition of the system



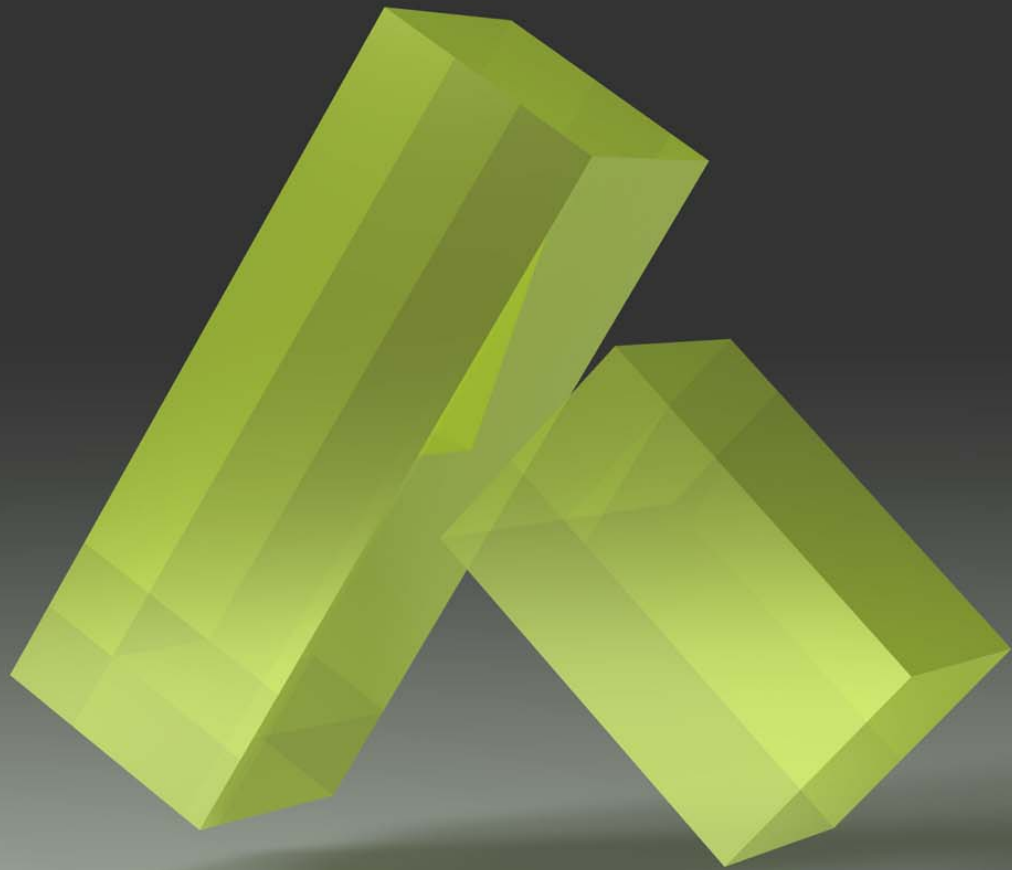
- ▶ ~6% of amorphous Si is enough to reduce κ by a factor of 20!
- ▶ Thermal anisotropy, the ratio of $\kappa_{\text{in-plane}}$ and $\kappa_{\text{out-of-plane}}$: between 4 and 6



Summary and Perspectives

- ▶ DFT has become a standard in materials research
- ▶ A vast variety of properties can be routinely calculated
 - structural, mechanical, thermodynamic, kinetic, electronic, optical, magnetic, and transport properties
- ▶ Latest developments
 - Simulation of alloys: Universal Cluster Expansion
 - Automated forcefields from quantum mechanical calculations
 - Automation of simulation protocols (Flowcharts)

**Better materials with
better simulations**



www.materialsdesign.com



MedeA[®] in Practice



MedeA[®] Software



MODELING & ANALYSIS

Builders: crystals, defects, interfaces, surfaces, molecules, nanostructures, polymers, amorphous materials

Analysis: geometry, band structures and DOS, electron and spin density, potential, Fermi surface, phonons, transition states, dynamics trajectories

Job Server

DATABASES

Experimental and Computed Structure and Property Data

ICSD

NIST Crystal Data

Pauling

Pearson

Computed

Task Servers

Mechanical

Thermal

Chemical

Kinetic

Electric

Optic

Magnetic

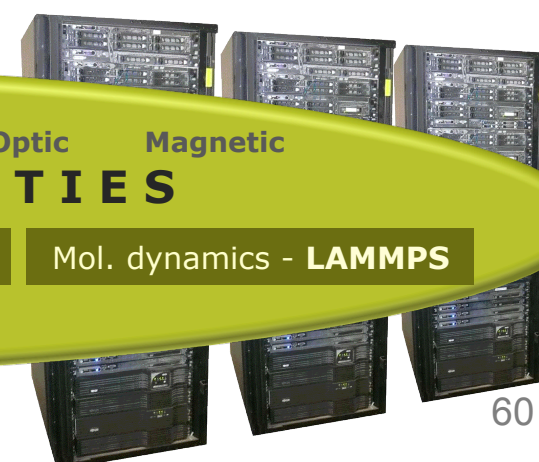
COMPUTATION OF PROPERTIES

ab initio QM - **VASP**

Semi-empirical - **MOPAC**

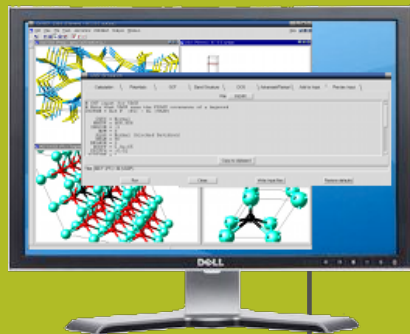
Monte Carlo - **GIBBS**

Mol. dynamics - **LAMMPS**





MedeA[®] Training Setup



User Interface

Model creation
and analysis of results

Local databases
(experimental and computed)

Local JobServer

Loaded with completed
results of many

- . Examples
- . Structures
- . Properties

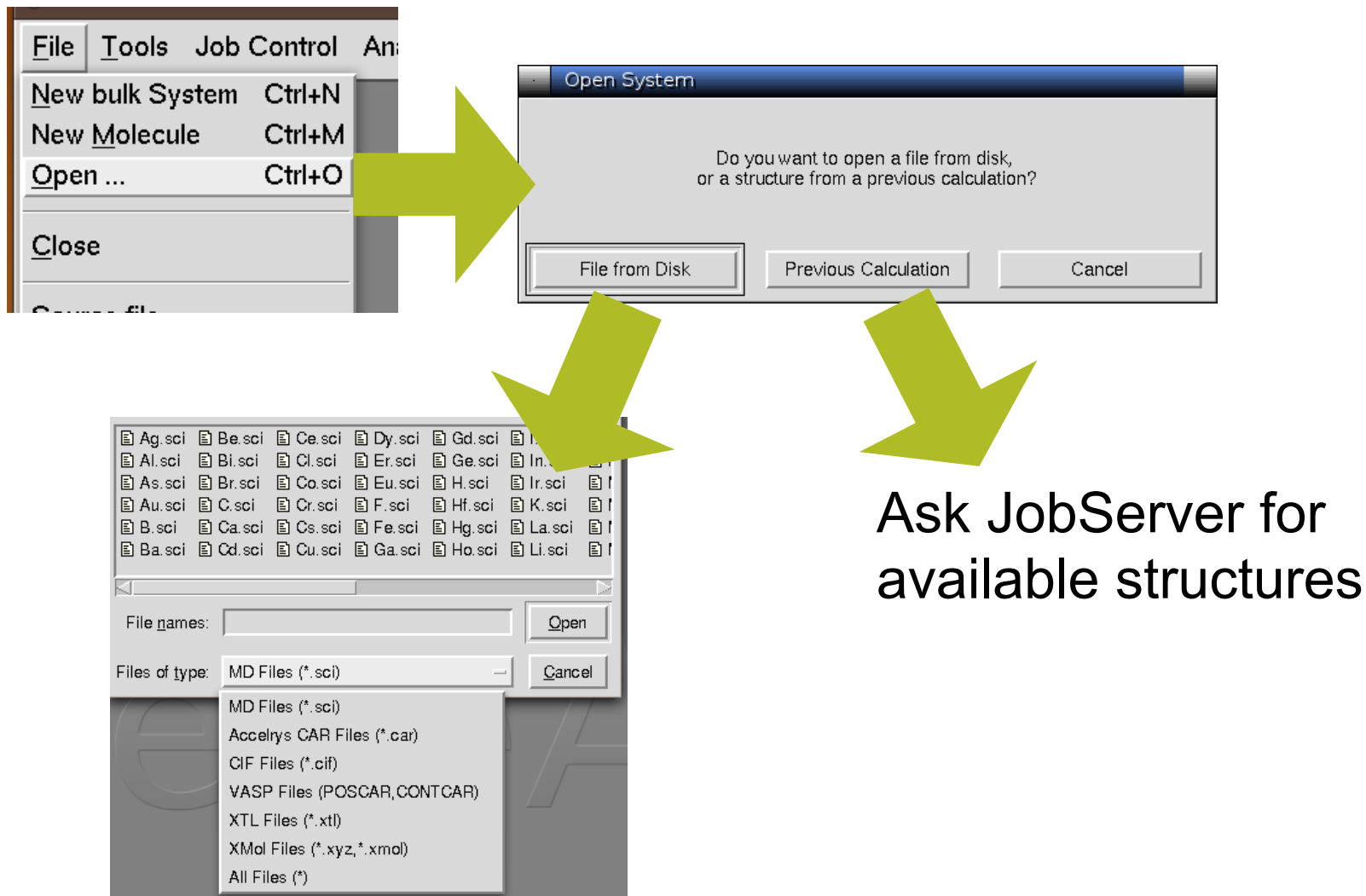
Local TaskServer

multiple core processor computers
for serial and parallel calculations



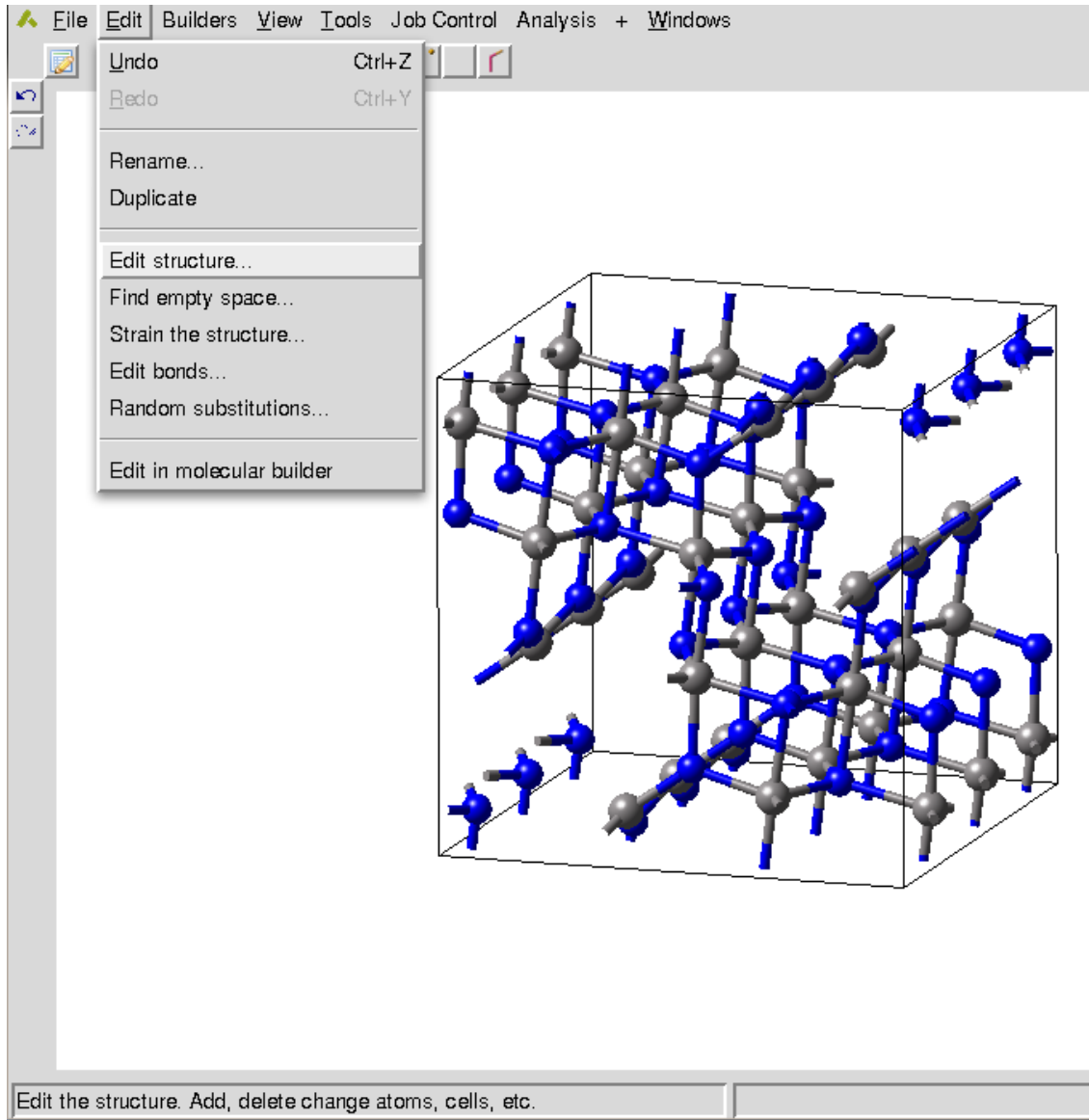
Access Structures

Load Structures









Crystal Structure Editor













- ▶ Change lattice parameters
- ▶ Raise/lower symmetry
- ▶ Atom properties
 - Move
 - Edit (Replace)
 - Add
 - Freeze coordinates
 - Initial magnetic moment
 - Mass



Keyboard Shortcuts

- ▶  - **Z** undo the last action
- ▶  - **A** select all atoms in the drawing area
- ▶  clear the atom selection
- ▶  delete all selected atoms
- ▶ **R/T/S/Z** press and hold down one of these keys to temporarily swap between the current mode and **Rotate/Translate/ Select/Zoom**

- ▶   + **R/T/Z** **R** 1°/**T** 0.1 Å/small **Z**
- ▶  +   + **R/T/Z** **R** 10°/**T** 1 Å/big **Z**
- ▶   + **R/T + S** **R**(→)/**T** selected atoms
- ▶   + **R/T + S** **R**(↑)/**T** selected atoms
- ▶  + one of the above **R**-axis/**T** ⊥ image plane



Loading Tools to Menu Bar

The diagram illustrates the process of loading a tool to a menu bar. On the left, a screenshot of the 'Tools' menu shows 'Forcefields' highlighted with a yellow circle. A yellow arrow points from this circle to a yellow circle around 'Forcefields' in the menu bar of a second screenshot on the right. A blue starburst with the text 'Left click' is positioned between the two screenshots, indicating the action performed.

Tools Menu (Left):

- InfoMaticA
- ElectrA
- VASP 5.3
- VASP 5.2
- VASP 4.6
- Forcefields**
- Gibbs
- LAMMPS
- Combi
- Automated Convergence
- Point Defect Analysis
- MPO
- Interfaces
- PrediBond
- Phonon
- Mechanical and Thermal Properties (MT)
- Electronics
- Transition State Search

Menu Bar (Right):

- Tools
- Job Control
- Forcefields**
- Analysis
- +
- Windows

Forcefields Sub-menu (Right):

- Read ...
- Choose
- Forcefield Editor

Forcefields Sub-sub-menu (Right):

- pcff
- ✓ pcff+



Flowchart: Complexity Made Simple

Start
Must for
all
flowcharts

LAMMPS

Clear
Delete
Edit...

Reading and writing flowcharts

Open ... Save ...

From job: ... Open

Add stages

Hill-Walpole Bounds
Mechanical Properties

Methods

Gibbs: Monte Carlo
Gibbs: Adsorption Isotherm
LAMMPS: Molecular Dynamics and Statics
MOPAC: Semiempirical QM
VASP 4: Density Functional Theory
VASP 5: Density Functional Theory

Building and Editing

Set Cell
Supercell
Amorphous Builder
Translate Atoms
Randomly Substitute Atoms

Forcefield

Job title: _____

Run Close

Read/save
flowcharts from/to
disk

Read flowcharts
of previous jobs

Click here to add
Stages to the left
side

Right-click on stages
opens context menu



JobServer – Web Interface

► Filter & Find

- User
- Status
- Time
- Number of Jobs to display

• Start Over

- Clean all results
- Start from fresh Input files

• Restart

- Use existing files
- Get files from completed tasks or redo missing tasks

Show all jobs meeting these criteria:

user is administrator root medea (use the ctrl key to select multiple users)

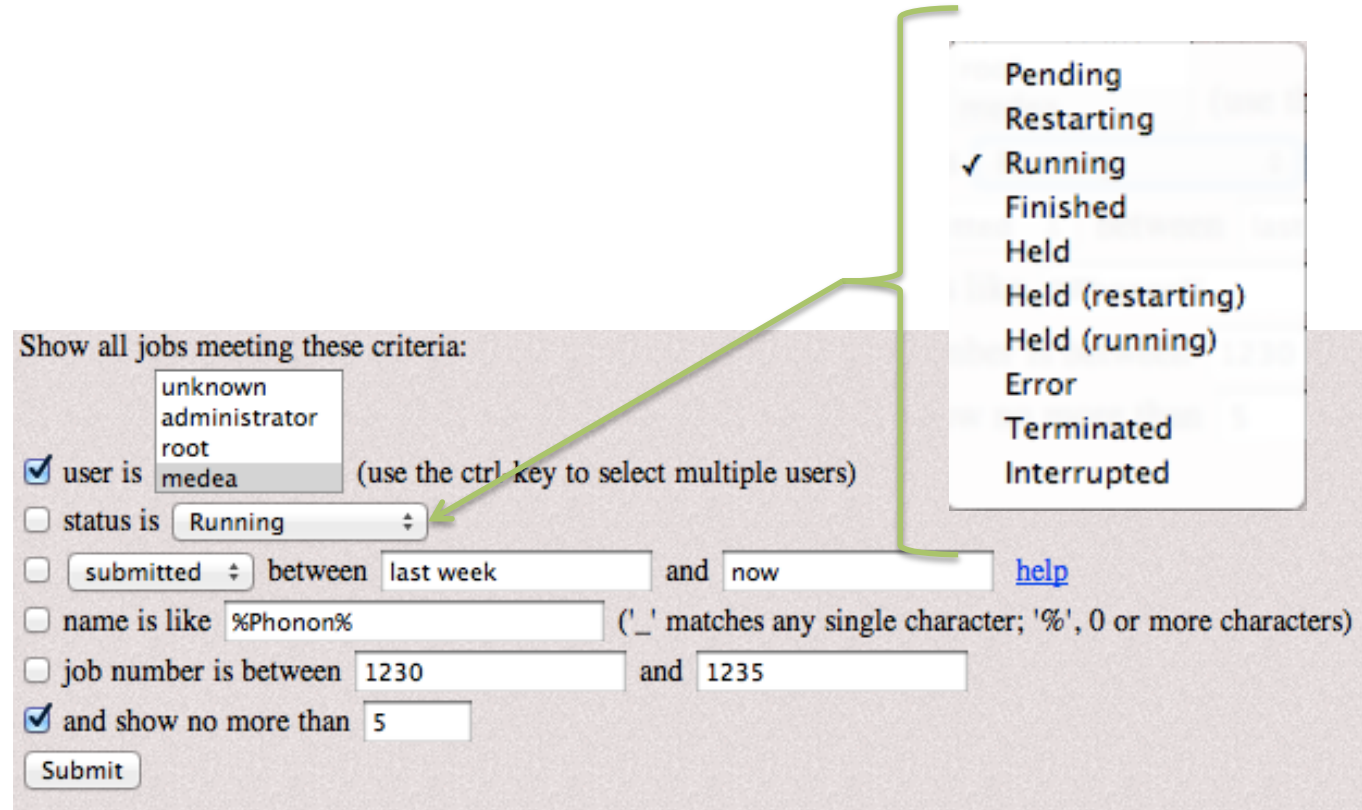
status is

submitted between and [help](#)

name is like ('_' matches any single character; '%', 0 or more characters)

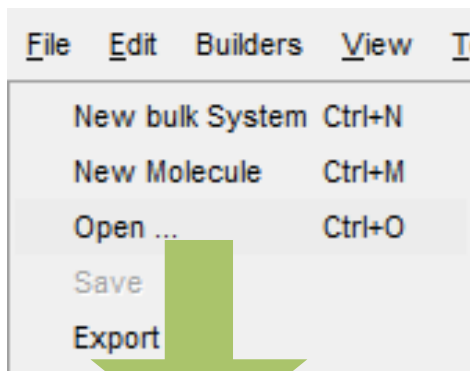
job number is between and

and show no more than





Retrieve & Analyze Results



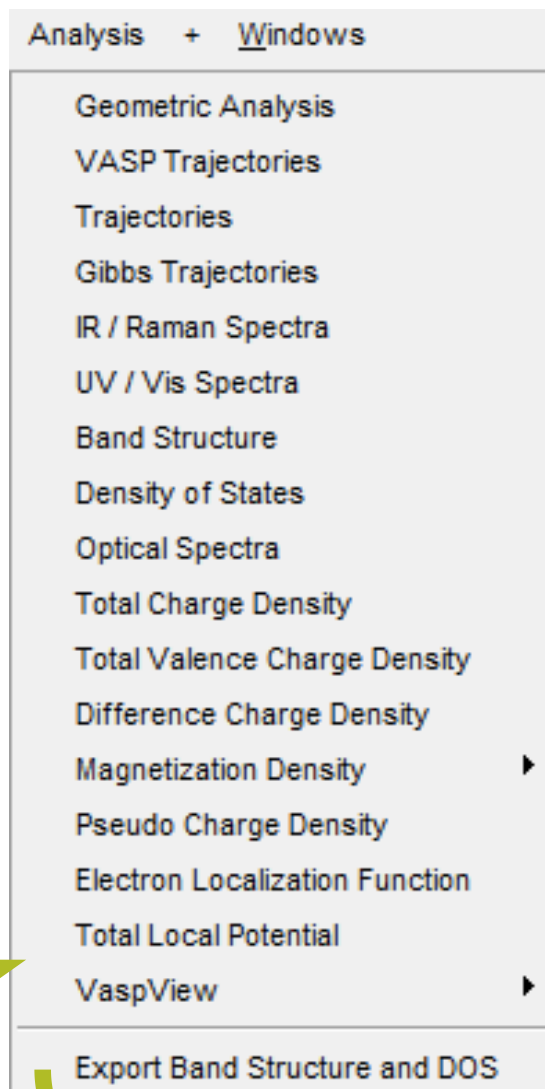
Do you want to open a file from disk,
or a structure from a previous calculation?

File from Disk

Previous Calculation

Cancel

Contact JobServer for
available results and data



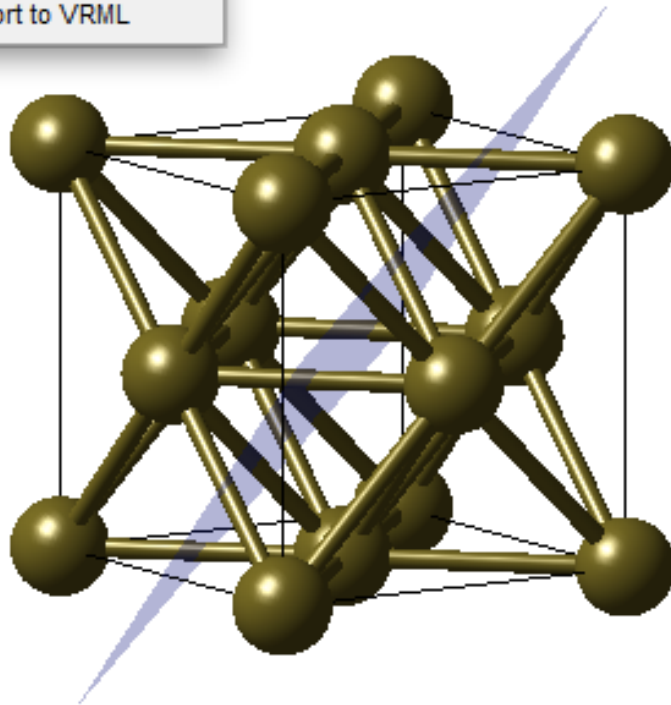
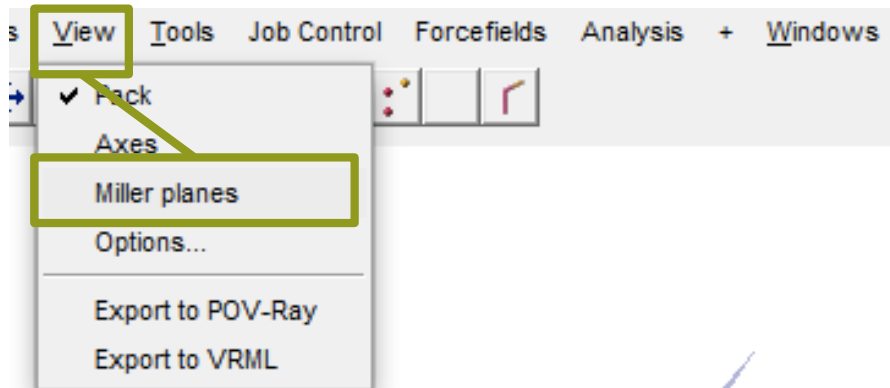
Calls Microsoft Excel macro
to create spreadsheet



Building Tools & Editors



Crystal Planes



► File → Open → File from Disk

- Browse to MD/Structures/Elements
- Load Au.sci , Ag.sci, Pb.sci, ...

► Display (1-11) Miller plane

- Only for your guidance
- No relevance in computation



Supercell Builder

► Builders → Build Supercells...

► Simple

- NxMxO box

► Automatic

- Equally in all directions
- In one direction only
- (h,k,l), range
- ... like surface builder

► Custom:

- display hexagonal crystal in orthorhombic box
- $a' = \{2 \ 1 \ 0\} a$
- $b' = b$
- $c' = c$

Supercell extends: in one direction only

Extension of cell

Direction x: 1

y: 1

z: 1

Angular tolerance (deg): 1.0

Range of cell: 30.0

Simple Automatic Custom

OK Cancel Apply



Structures & Databases



MedeA[®] InfoMaticA

▶ Interface to the structure databases

- ICSD ICSD (FIZ Karlsruhe, Germany)
- Pauling (MPDS Projects, Switzerland)
- Pearson (ASM International, USA)
- NCD (NIST, USA)
- COD (Cryst. Open Database)

▶ More than **500'000** records in total

▶ Binary Phase Diagrams (Pauling)

▶ All records: lattice parameters (a, b, c, α , β , γ)

▶ Atomic coordinates depend on *structure type*

▶ Available *structure types*:

Type	Atomic coordinates	Site occupancy n
complete	all	1
disordered	over-complete	$0 \leq n \leq 1$
Missing atoms	incomplete	$0 \leq n \leq 1$
unknown	none	--

▶ Information on

- Structures
- Lattice parameters
- Literature Data
 - Experimental setup
 - Phase information
- Powder pattern
- Coordination plots
- Pair correlation function



InfoMaticA: Search Criteria

Open InfoMaticA: Tools → InfoMaticA, InfoMaticA → Search ..., panel Search Criteria

The screenshot shows the 'Search Criteria' panel in InfoMaticA. The panel has a tabbed interface with 'Search Criteria' selected. Below the tabs, there are two 'Require that' buttons, a 'Formula' dropdown menu, and a 'contains any number of' dropdown menu. The 'Formula' dropdown is open, showing a list of search criteria. The 'Advanced' option is circled in green. A mouse cursor is hovering over the 'cell' option, which is also circled in green. A callout box with a mouse cursor icon and the text 'Add new criterion' points to the '--Add new criterion' button. Another callout box with a mouse cursor icon and the text 'Select more criteria' points to the 'Advanced' option. The list of search criteria includes: Database ID, Formula, Number of Elements, Structural Completeness, Author, Title, Systematic Name, Mineral Name, Remark, cell, chemical, chemical formula, citation, database, exptl crystal, protocol, refine, structure, symmetry, volume, angle alpha esd, angle alpha, angle beta esd, angle beta, angle gamma esd, angle gamma, formula units Z, length a esd, length a, length b esd, length b, length c esd, and length c.



InfoMaticA: Search Mask

The screenshot shows the InfoMaticA software interface with several callouts highlighting key features:

- Pauling binary phase diagrams**: A callout pointing to the 'Pauling' menu option in the top-left corner.
- Show binaries matrix**: A callout pointing to the 'Show binaries matrix' option in the 'Pauling' menu.
- Sort functions**: A callout pointing to the 'Sort Ascending' and 'Sort Descending' options in a context menu.
- Add/Remove properties to table**: A callout pointing to the 'Delete' and 'Insert...' options in a context menu.
- View**: A callout pointing to the 'View' option in a context menu.
- Load structures into viewer**: A callout pointing to a mouse icon in the top-right corner.

The main window displays a table of search results with columns for ID, Completeness, space group, and structural formula. Below the table, there are tabs for 'Search Criteria', 'Detailed Information', 'Coordinates', 'Geometry', 'Coordination', 'Pair Correlation', and 'Powder pattern'. The 'Search Criteria' tab is active, showing a list of criteria with fields for 'Require that', 'Formula', and 'atoms of'. A dropdown menu is open for the 'atoms of' field, showing options like 'Complete', 'Missing Atoms', 'Disordered', and 'None Available'. At the bottom, there are 'Run search' and 'Clear' buttons.

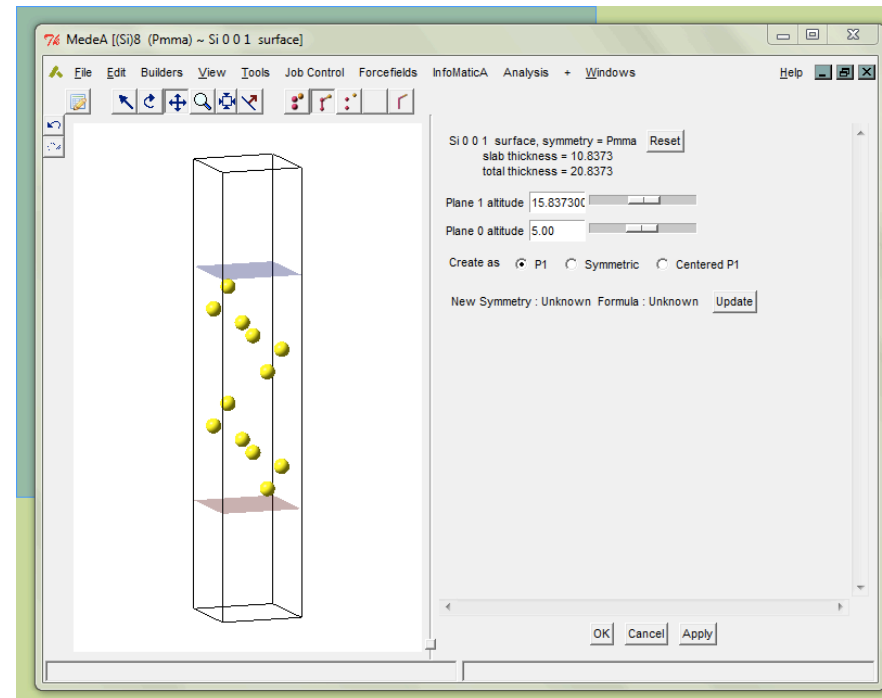
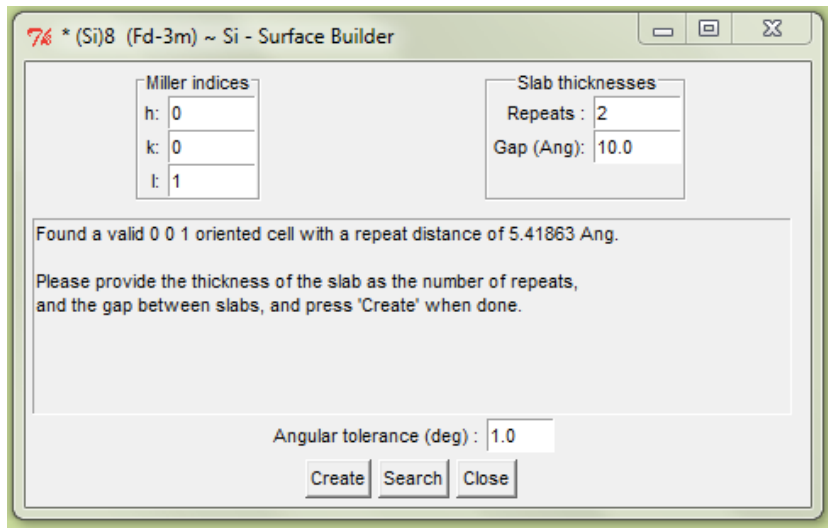


Surfaces



Si(001) Surface

- Define
 - Orientation
 - Repeat units
- Search
- OK

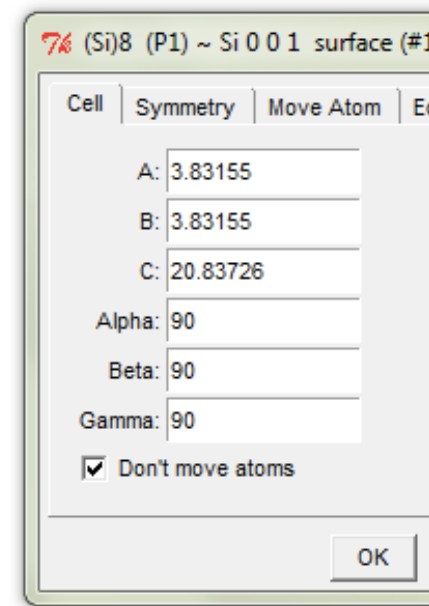
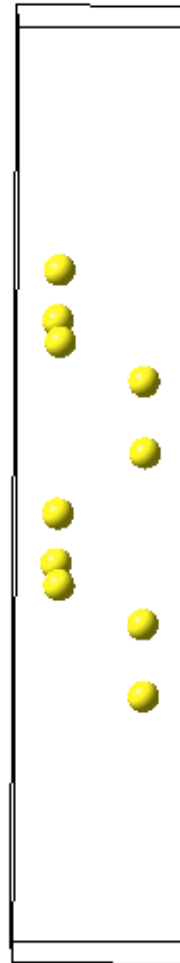


job #190



Si(001) Surface

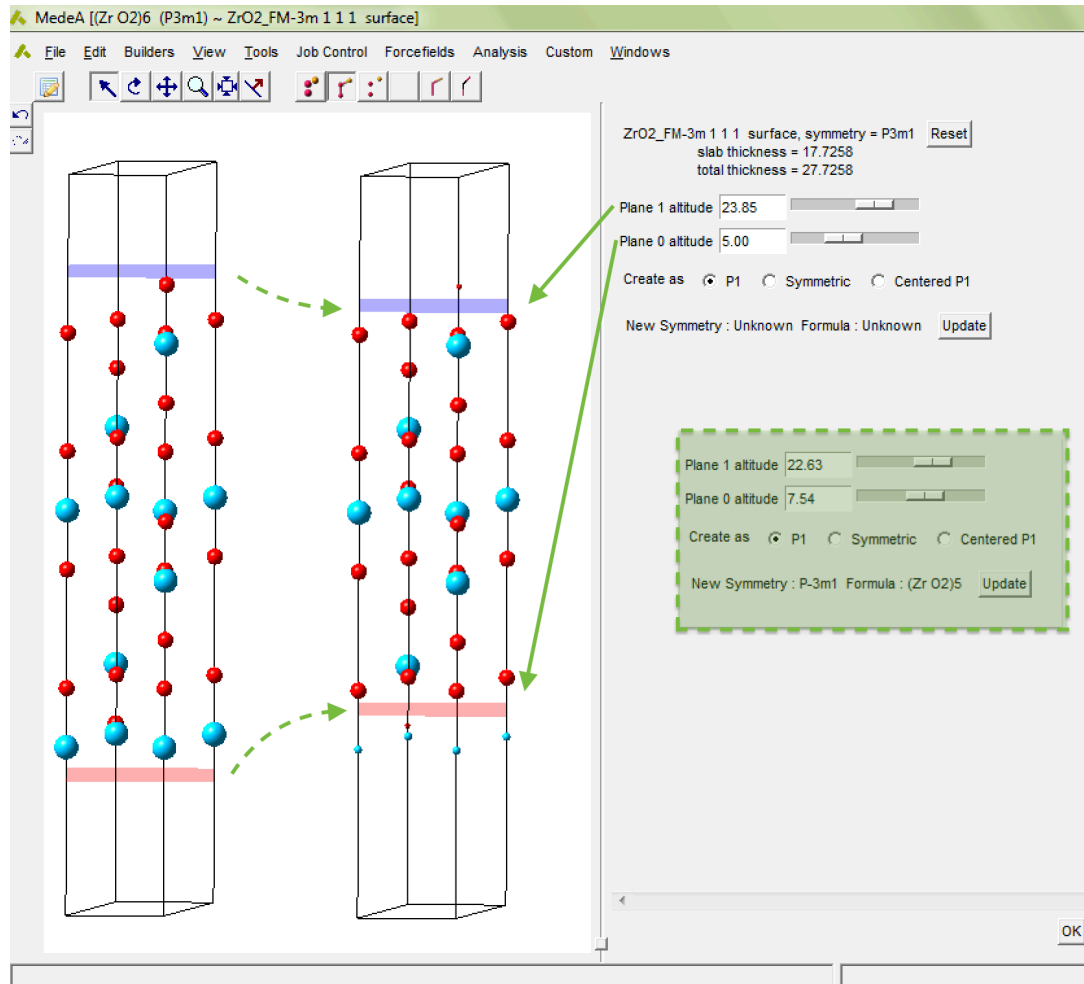
- ▶ Builders>>Build Supercell
- ▶ 5x5x1 supercell
- ▶ Edit >> Cell
 - Menu or
 - Right-click
- ▶ Expand cell:
 - $c=40 \text{ \AA}$
- ▶ Don't move atoms



job #190



Surface Termination



Move planes to exclude atoms

Tilt cell a little bit to see red and blue planes

Update **symmetry** for Formula: (ZrO₂)

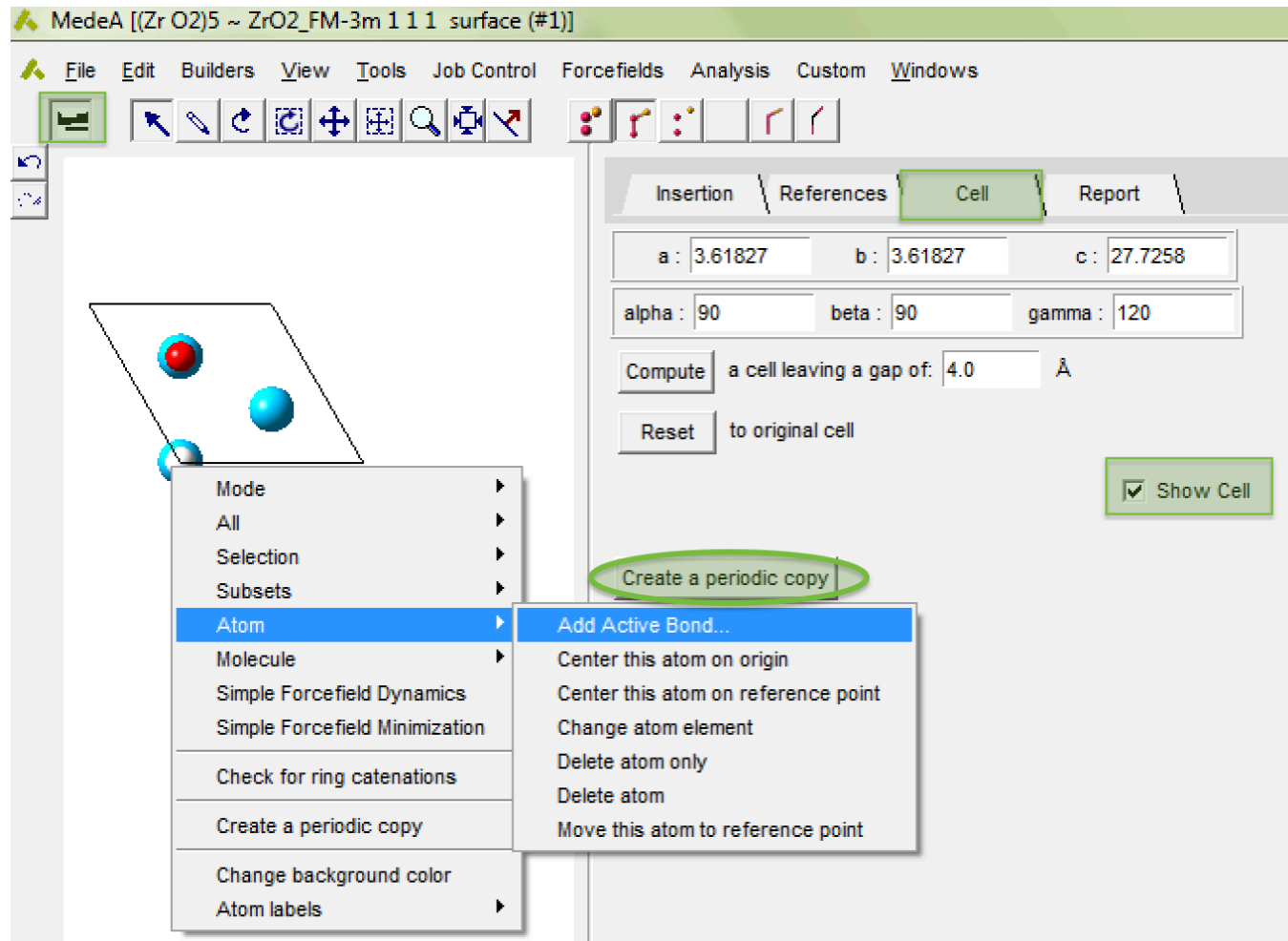
Impose symmetry?
Centered P1 moves slab into middle of cell (no effect on calculations)

Avoid polar surface slabs:
O termination on top,
Zr termination on bottom

Finish with **OK**



Preparing Surface Atoms



Click on **periodic table** icon

Model boundaries:
In Cell tab check
Show Cell

Select atom, right-click
Atom >> Add Active Bond...

Create a periodic copy when done

Surface Hydrogenation

The screenshot shows the Medea software interface. The main window displays a molecular model of a surface with atoms represented by spheres. A red dashed circle highlights a specific atom on the surface. A red arrow points from the top-left corner of the interface to the red dashed circle. A green arrow points from the 'Hydrogenate' button in the control panel to the red dashed circle. Another green arrow points from the text 'works on all active bonds' to the 'Hydrogenate' button. The control panel includes a periodic table, a 'Clean' button, and buttons for 'Fragments', 'User fragments', 'Hydrogenate', and 'Passivate'. The 'Hydrogenate' button is highlighted in green.

Hydrogenate adds H to all active bonds

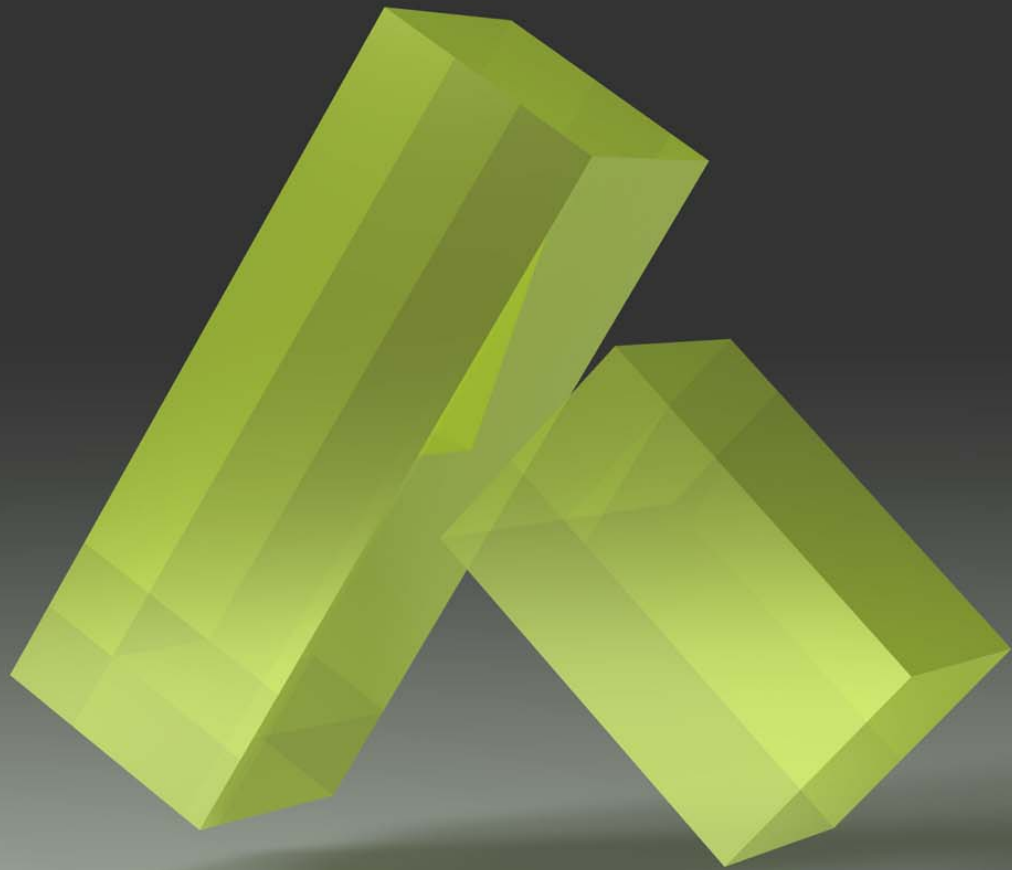
You can use any atom or group to **Passivate**

Use the sketch pen to draw molecules

Right-click: **Selection >> Simple Forcefield Minimization**

And don't forget: there is **Undo**

**Better materials with
better simulations**



www.materialsdesign.com