Ab initio modeling of thermoelectric materials

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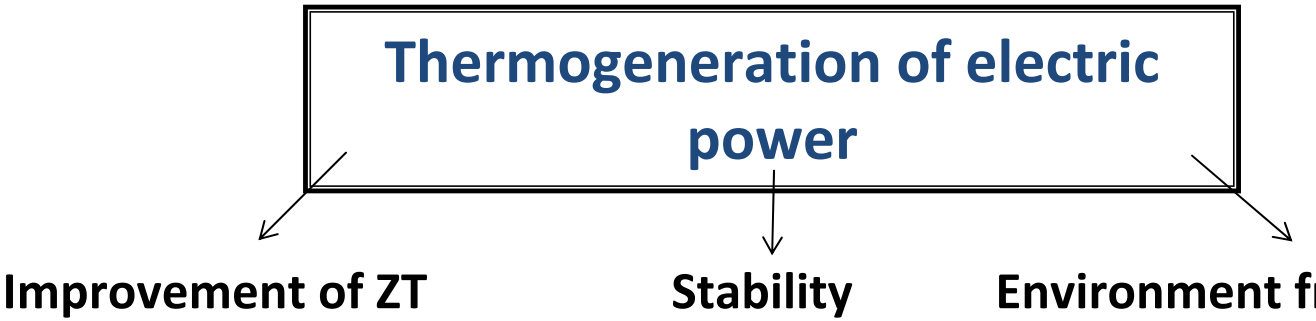
Study of TE materials in the C2M group



Double approach

Experimental

- Synthesis
- Structural characterization
- Thermodynamic experiments
- Thermoelectric experiments
- Spectroscopies

Simulations

- Ab-initio : structural relaxation
- Ab-initio : mechanical properties
- Ab-initio : electronic properties
- Ab-initio : phonons
- Ab-initio : defects
- Calphad (phase diagrams)

Numerical simulation tools

- Stability & electronic properties : VASP, MindLab, Wien2k

- Defect calculations : VASP + « home made » program

- Mechanical properties : VASP + program based on the Debye model

- Lattice dynamics : PHONON, Phonopi

- Thermal properties : PHONON, molecular dynamics + specific program to be developed

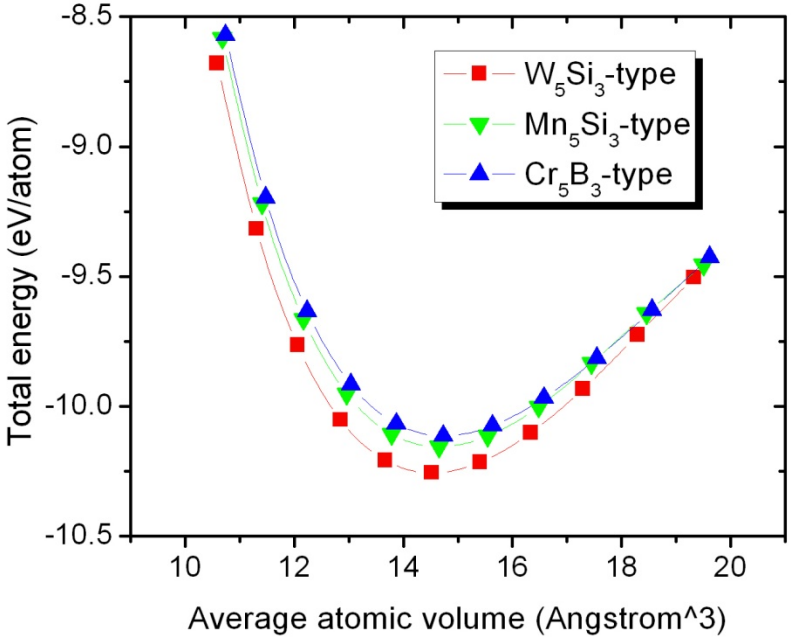
- Phase diagrams : CALPHAD

Numerical simulations : structural stability

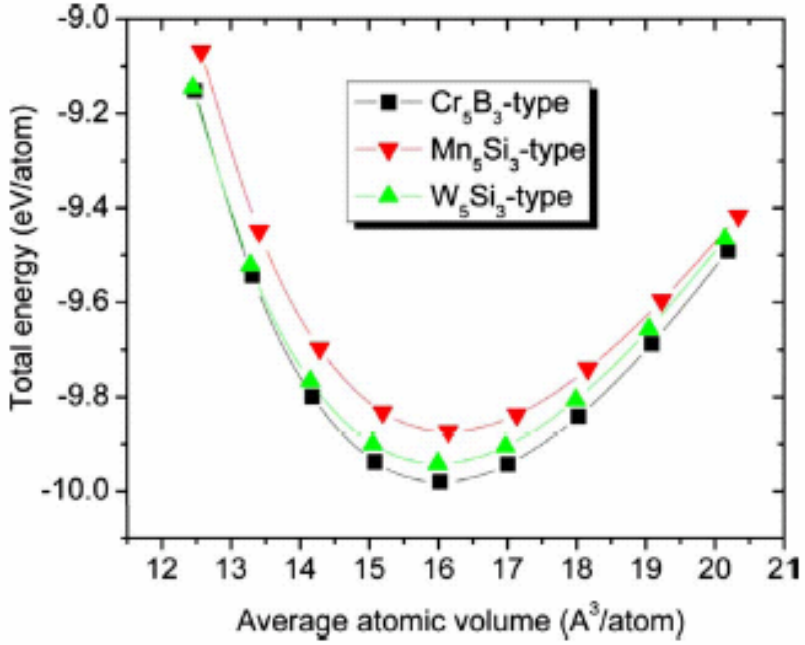
Phase stability of thermoelectric materials up to very high temperatures, is often required

Ex : M_5Si_3 with M=Ta et W

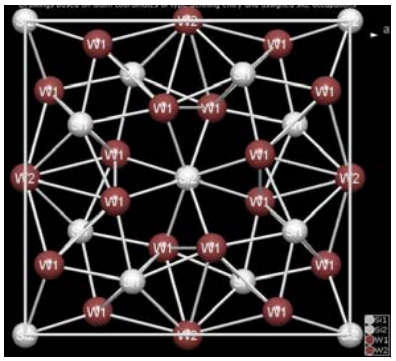
W_5Si_3



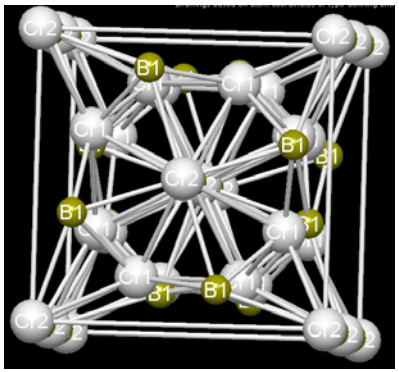
Ta_5Si_3



W_5Si_3 ($D8_m$) the stable structure



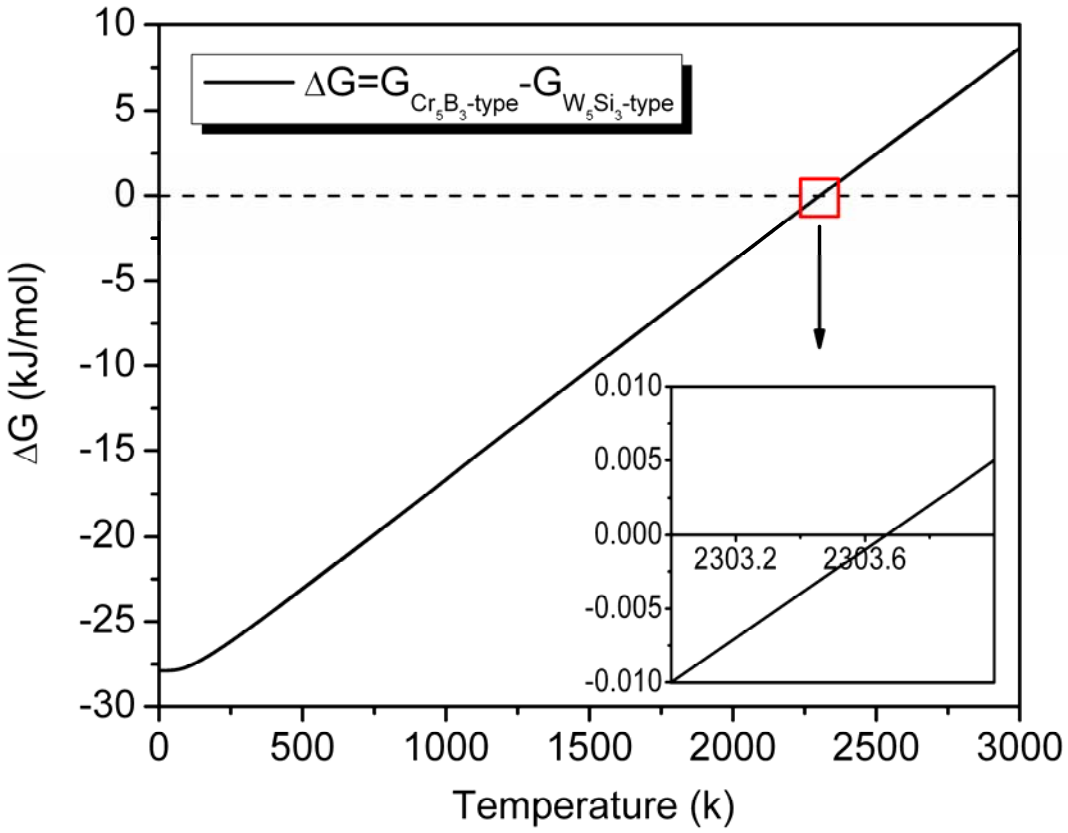
*(Intermetallics **18**, 688 (2010))*



Cr_5B_3 ($D8_1$) is the stable structure

Numerical simulations : structural stability

Cr_5B_3 – W_5Si_3 phase transition for Ta_5Si_3



the simulated transition temperature is 2304 K (experimental T = 2433 K)

*(Phys Rev B **80**,104103 (2009))*

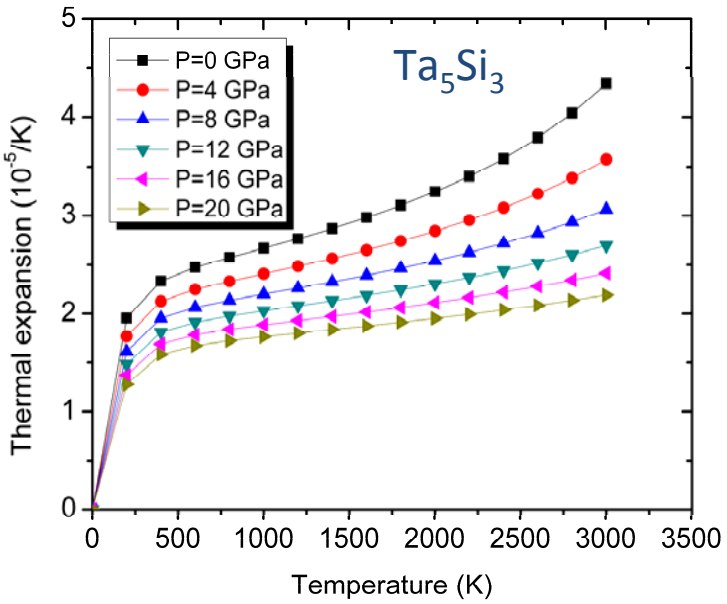
Numerical simulations : mechanical properties

High temperature gradients betweeen the cold and hot parts of a TE junction ⇒ the thermal expansion coefficient should be small to limit the mechanical constraints
⇒ the study of the mechanical properties is important

	Ta_5Si_3	W_5Si_3
B (bulk)	222.11 GPa	265.6 GPa (exp. : 274.5 GPa)
G (shear)	130.57 GPa	119.1 GPa
E (Young)	327.53 GPa	312 GPa
ν (Poisson)	0.254	0.31
ductility ratio *B/G*	1.7	2.31

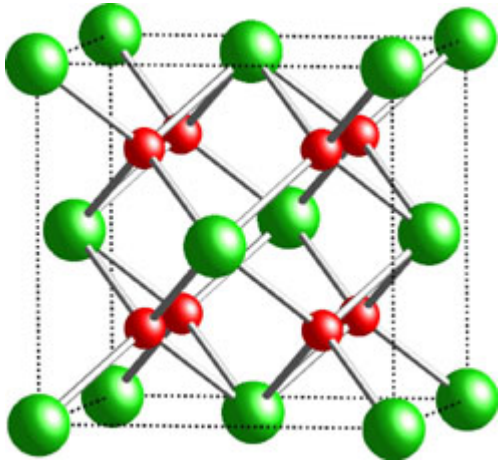
Ductile if > 1.75

Debye Model ⇒ study of the properties vs temperature and pressure



Numerical simulations : structural stability

Mg_2Si crystallizes in the cubic anti-fluorite structure under ambient conditions

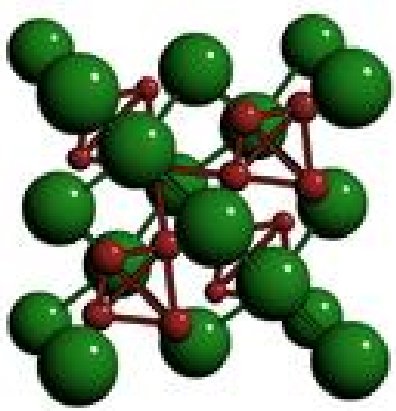


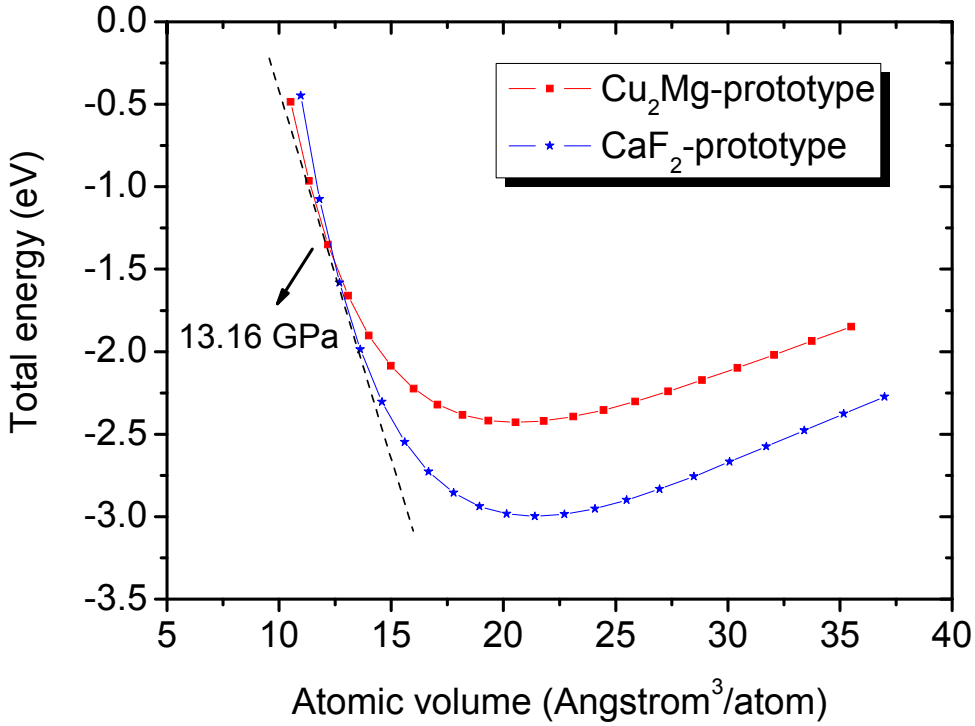
Phase	Calculation type or experiment	Structure type	Lattice parameters			Formation enthalpy (eV/atom)
			a(Å)	b(Å)	c(Å)	
Mg_2Si	GGA-PBE (PAW)	CaF_2	6.356	6.356	6.356	-0.162
	LDA (PAW)		6.2566	6.2566	6.2566	-0.176
	GGA-PBEsol (AE)		6.3224	6.3224	6.3224	-0.157
	Experiment		6.351	6.351	6.351	-0.15 → -0.3

mechanical properties (GPa)	C_{11}	C_{12}	C_{44}	B
PBE	118	24	46	55
EXPT.	126	26	48.5	59

Numerical simulations : structural stability

Experimentaly a Cu_2Mg Laves structure has been predicted for Mg_2Si at room temperature and ambient pressure : numerical confirmation ?





The Laves phase becomes stable at high pressure (13 GPa) $\Rightarrow$ it is unlikely to observe this phase under ambient conditions

Numerical simulations : formation energies of defects

The relative formation energies of intrinsic defects are important to know the potential doping mechanisms of TE materials.

Ex : Mg_2Si (supercell : 96 particles)

Defect in Mg_2Si	PW91 (eV/defect)	PBE (eV/defect)
V^{Mg}	1.54	1.53 (1.84)
V^{Si}	2.26	2.21
Si^{Mg}	1.66	1.55
Mg^{Si}	2.83	2.83
I^{Si}	2.57	2.39 (2.63)
I^{Mg}	1.40	1.26 (1.84)
V^{MgSi}	1.16	1.15
V^{Mg2Si}	1.42	1.33

( ) no relaxation

$$\Delta_f H = \Delta_f H^\circ + \sum_D H_D x_D$$

H_D the enthalpy of formation of the defect D

x_D its atomic concentration.

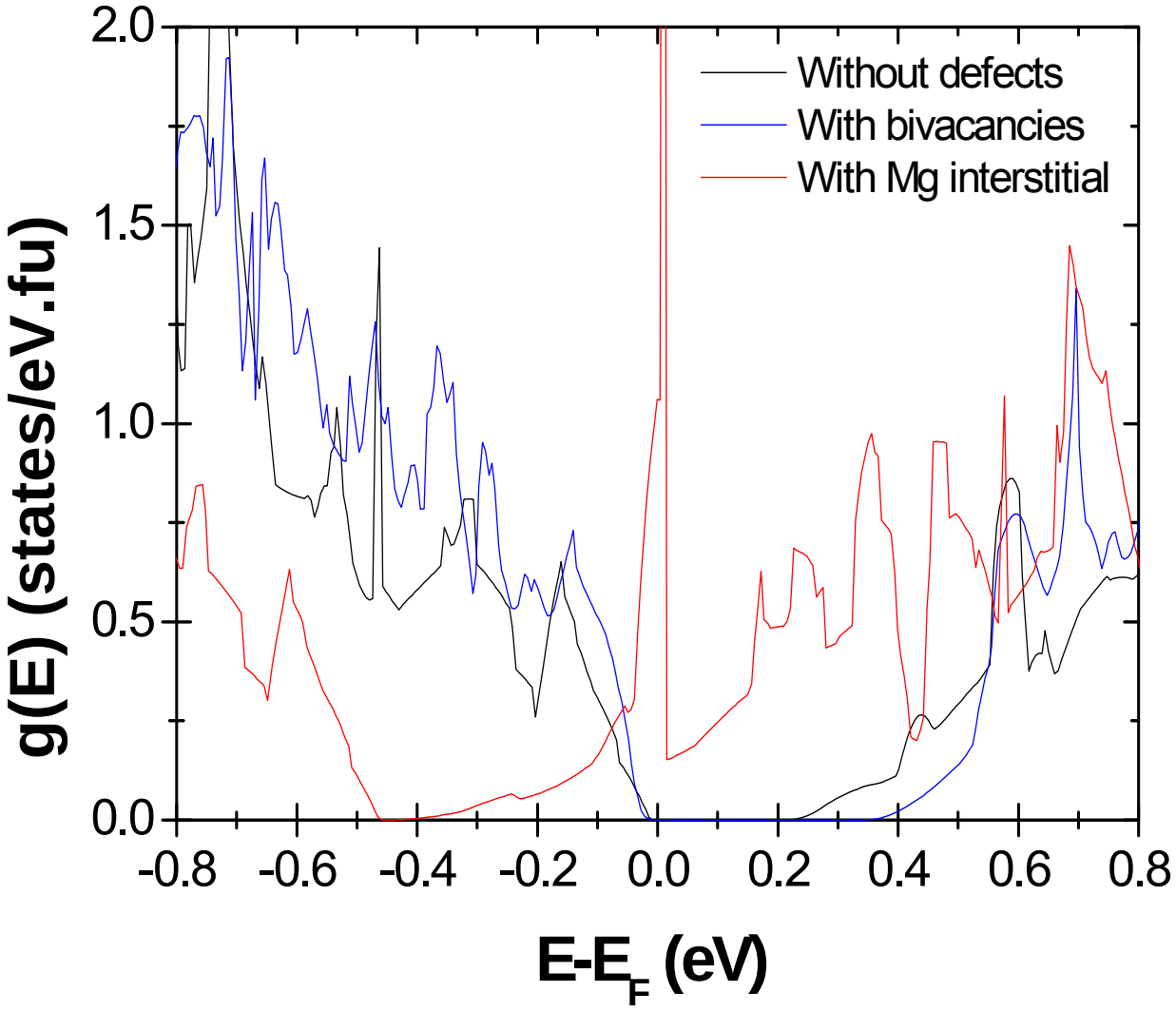
$\Delta_f H^0$ is the enthalpy of formation of the perfectly ordered stoichiometric alloy

→ the most favorable defects are coherent with the n type of Mg_2Si

→ it is mandatory to relax the structure to obtain correct results

Numerical simulations : electronic properties

Effect on the density of states



→ the calculated gap (0.22 eV) is smaller than the experimental value (0.7eV) as expected with GGA calculations

→ the most favorable defects are coherent with the n type of Mg_2Si

→ the defect content is ↑
⇒ Mg_2Si becomes metallic

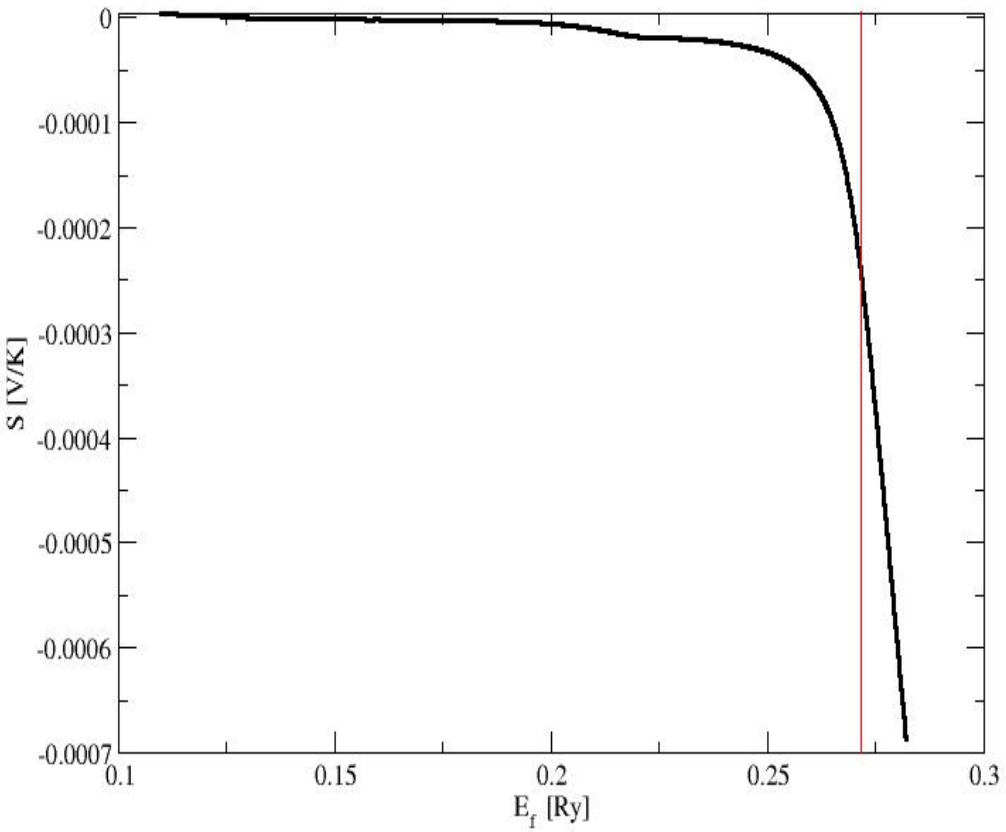
Numerical simulations : thermoelectric properties

Seebeck coefficient with BoltzTrap

* We look up the Fermi level in the W2K output file to determine the Seebeck voltage of the pure undoped crystal for Mg_2Si
* In BoltzTraP, we calculate the Seebeck voltage as a function of Fermi level
* ~-250 μV/K at 300K

(exp: -(260-270) μV/K

Choi et al., Curr. App. Phys 2011)

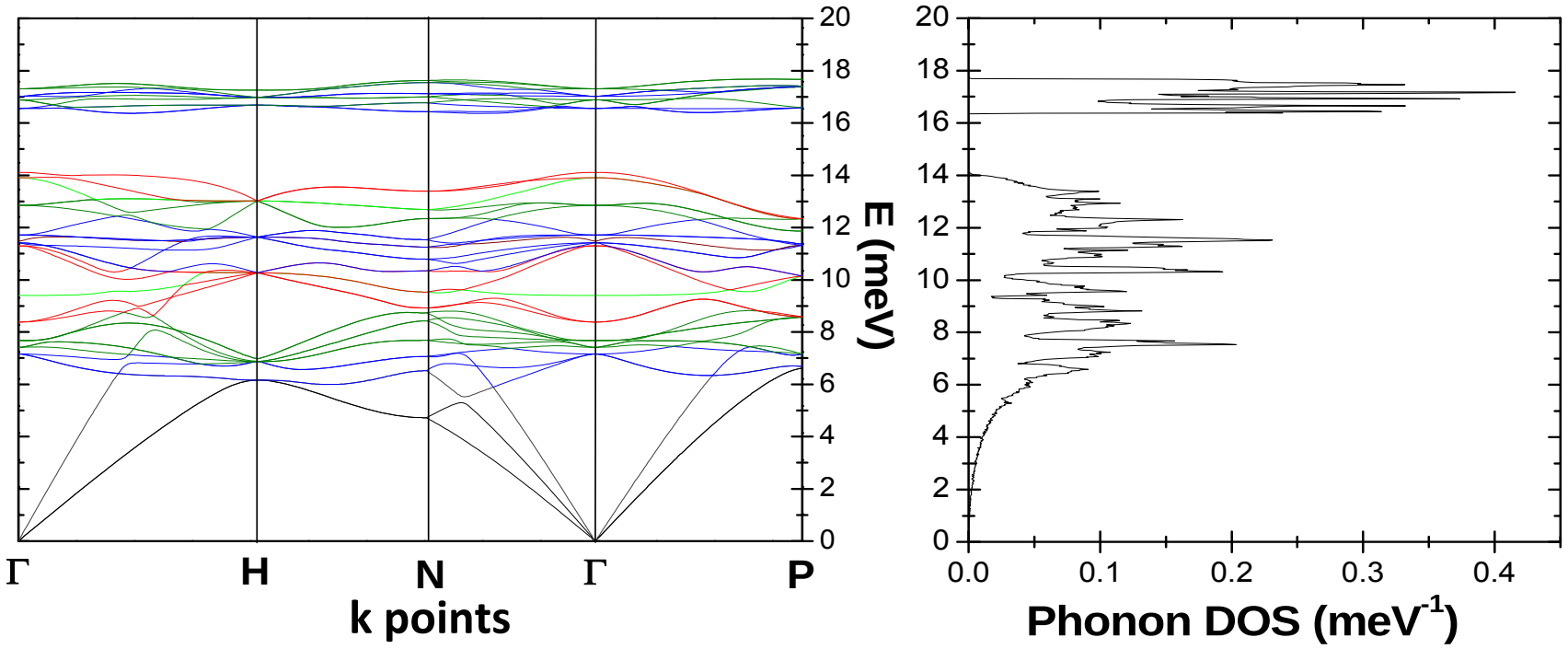


Numerical simulations : lattice dynamics

Search of materials with a small thermal conductivity ⇒ one needs to know the vibrational properties (phonons)

Ex: cubic materials with anti-Th_3P_4 structures La_4Sb_3 ($\kappa \cong$ 3-4 W/m.K ⇒ $\kappa_L \cong$ 1 W/m.K)

VASP + PHONON (supercell) ⇒ phonon dispersion curves + VDOS of La_4Sb_3 :

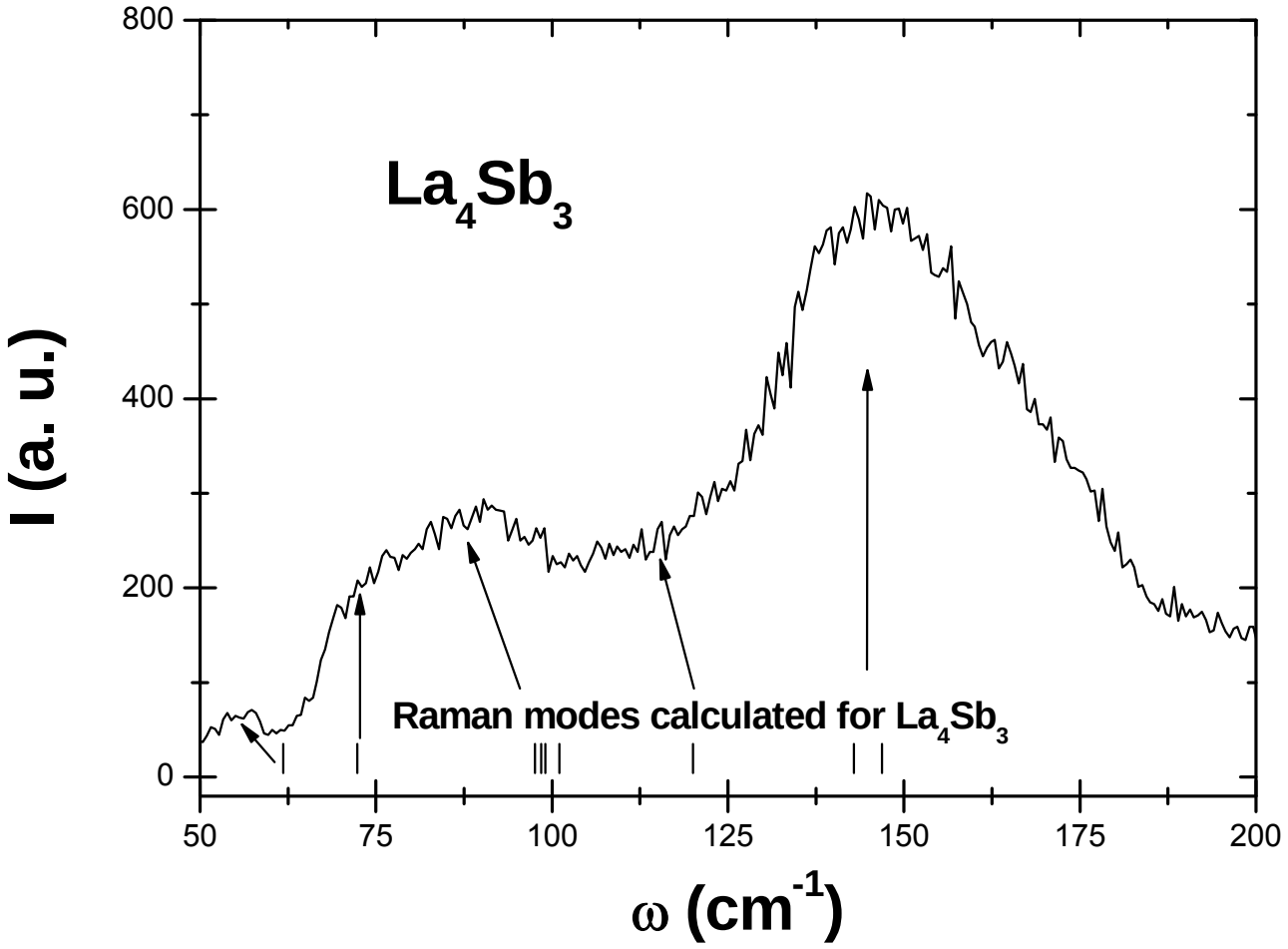


Hybridization between acoustic modes and low energy optic modes ⇒ the heat transfer is hindered ⇒ small thermal conductivity

(JEM (2011), Calphad (2011) sous presse)

Numerical simulations : lattice dynamics

Comparison with Raman spectrum :

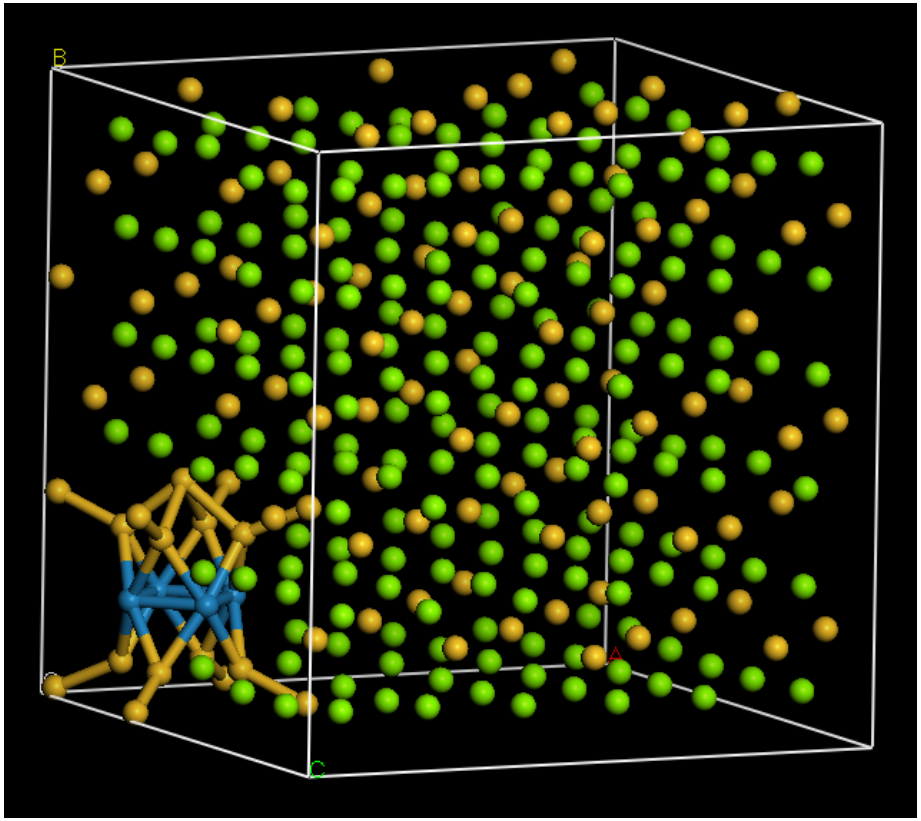


Relative good agreement between the modes obtained with Phonon and the Raman spectrum

Numerical simulations : nanoinclusions

Mg_2Si + metallic inclusion

Supercell calculations : 324 particles



Conclusions

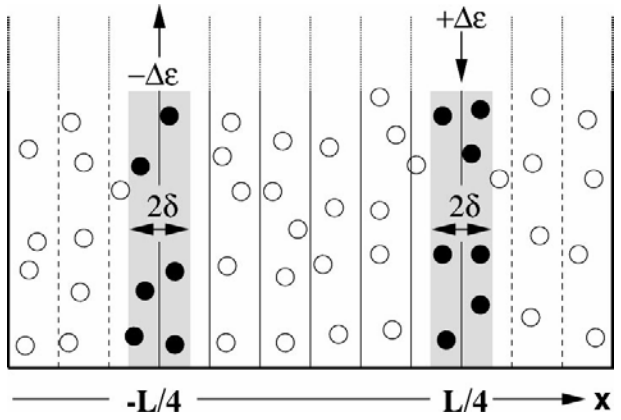
→ Ab initio simulations permit to perform bandstructure engineering of materials in order to propose the best materials exhibiting:
- good electronic properties
- small thermal conductivities
- good mechanical properties

⇒ simulations are the first step for the design of new efficient thermoelectric materials
- choice of the dopant
- effect of the nanostructuration

→ Needs to be done : calculation of the thermal conductivity
- direct calculation : molecular dynamics
with « hot » and « cold » plates in the cell
⇒ CPU time ↑

- Green-Kubo relations (MD)

- DFPT



Thank you for your attention.