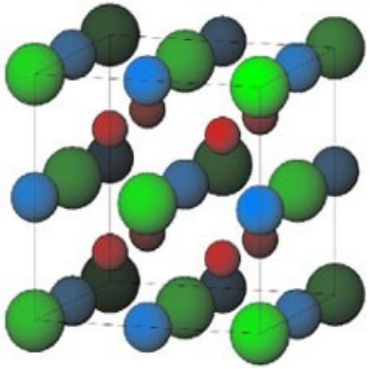
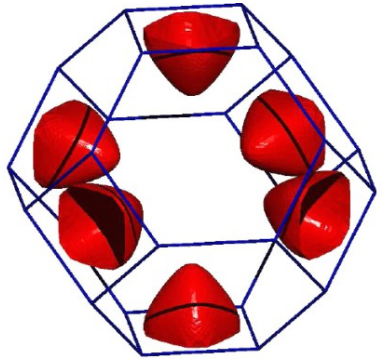


$$G = G_0 + G_0 V G$$



First principles calculations of electronic structure and physical properties

superconducting, thermoelectric,magnetic, magnetocaloric behaviors in intermetallic compounds with chemical disorder

Katedra Fizyki Materii Skondensowanej WFIS AGH (D10, III p.)

Grupa obliczeń struktur elektronowych

prof. S. Kaprzyk, prof. J. Toboła

dr K. Kutorasiński, dr B. Wiendlocha

mgr P. Zwoleński (doktorant)

AGH

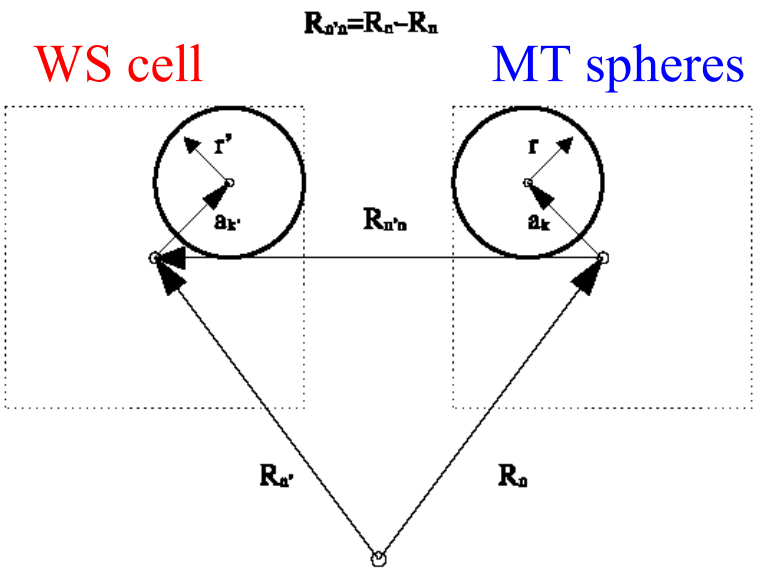
Multiply scattering theory *vs.* Korringa-Kohn-Rostoker (KKR) method

$$G = G_0 + G_0 V G.$$ Dyson equations

$$V = \sum_i v_i.$$ Crystal potential

$$G_0 = \frac{1}{E - H}$$ Free-electron GF

Computational geometry



T - scattering operator for many potentials

$$T = V + V G_0 T \qquad T = \sum_{i,k} [v_i \delta_{ik} + v_i \frac{1}{E - H_0 - v_i} \sum_{m \neq i} (v_i \delta_{mk} + v_m \frac{1}{E - H_0 - V} v_k)]$$

$$T = \sum_{i,k} T^{i,k},$$

$T^{i,k}$ – path scattering operator between *i* and *k* scattering centres

$$T^{i,k} = t_i \delta_{ik} + t_i G_0 \sum_{m \neq i} T^{m,k}$$

t - scattering operator for single potential v_i

$$t_i = v_i + v_i G_0 t_i.$$

KKR for ordered compounds

Approaches

* Reasonable computational time for systems with unit cell below 100 atoms.

* Full form of crystal potential (no restricted to spherical); LDA(+U).

* Semi-relativistic approach (core electrons – relativistic, valence electrons – nonrelativistic).

* Fully-relativistic approach (all electrons from Dirac eq).

* Magnetic effects (spin & orbital contributions) accounting for different magnetic moments arrangements.

Output

* Density of states (total & *s, p, d*, … for inequivalent atoms).

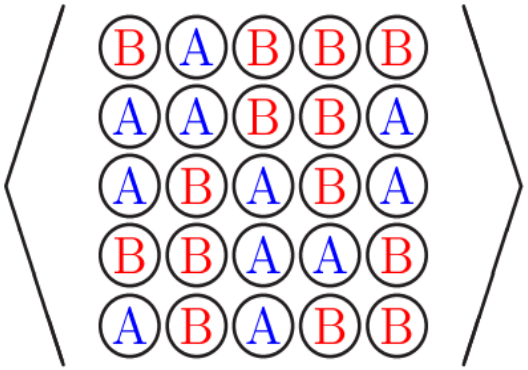
* Electronic dispersion curves & Fermi surface.

* Magnetic moments (total & inside Voronoi polyhedra; spin & orbital) for different magnetic structures.

* Total energy of compound (and all contributions).

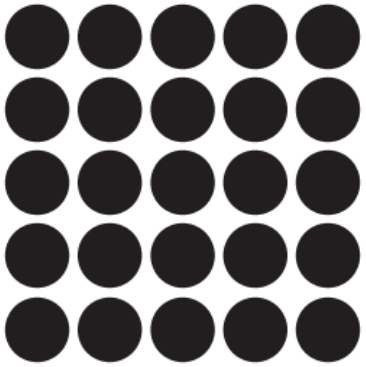
KKR-CPA method & complex bands

Disordered alloys: ~~periodic~~ - Coherent Potential Approximation (CPA):



CPA medium

=



CPA condition

$$c_A T^A + c_B T^B = T^{CP}.$$

In multi-atomic systems more complicated !

$$T^{CP}_{k'\sigma'L',k\sigma L} = \frac{1}{N}\sum_{\mathbf{k}\in BZ}\left[\tau^{-1}_{CP} - B(E,\mathbf{k})\right]^{-1}_{k'\sigma'L',k\sigma L}$$

CPA crystal - restored periodicity

- **price: complex potential**

Present version of fully self-consistent KKR-CPA code allows for:

- treatment of **many atoms** on the same disordered site (< 60 atoms per unit cell).
- calculation of **electronic structure of dopants** (very low concentration),
- calculation of **extra point defects** in crystals (vacancy, anti-site, etc.)
- calculation of **spin dependent electronic structure** (magnetism).

KKR-CPA for disordered alloys

Approaches

* Reasonable computational time for systems with unit cell below 60 atoms.
* *Muffin-tin* form of crystal potential (LDA).
* Semi-relativistic approach (core electrons – relativistic, valence electrons – nonrelativistic).
* Spin-dependent effects taken into account.

Output

* Density of states (total & *s, p, d*, … for inequivalent atoms).
* Electronic dispersion curves for alloys (complex energy).
* Magnetic properties (total & inside MT spheres).
* Total energy of alloy (and all contributions).

KKR & KKR-CPA strategies

Crystal structure

- atoms distribution in the unit cell of alloys
- concentration of elements on crystallographic sites
- possible point defects if available
- dilatation/contraction of cell to mimic temperature effects

KKR-CPA

Fast

Rough determination of ground state properties of $A_xB_yC_{1-x-y}$ (metal/semiconductor; magnetic/non-magnetic) & their evolution with alloy composition

Medium

Attempts to improve requested properties of new materials $A_xB_yC_{1-x-y}$ via substitution with novel elements *D*

Slow

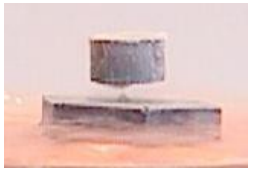
More sophisticated analysis of physical properties (Fermi surface properties governing electron transport, electron-phonon coupling, different magnetic orderings of magnetic moments); role of doping

Attempts to establish „electronic phase diagrams" for ternary or pseudo-quaternary systems, tending to predict (or **not to miss**) new properties.

Tematy prac doktorskich 2015

- Badanie struktury elektronowej i oddziaływania elektron-fonon w nadprzewodzących izolatorach topologicznych (*lub inna grupa materiałów*); *J. Toboła & B. Wiendlocha*
- Implementacja nowych potencjałów wymienno-korelacyjnych w metodzie KKR-CPA dla układów złożonych; *J. Toboła & B. Wiendlocha*
- Teoretyczne poszukiwania nowych stopów termoelektrycznych i optymalizacja układów znanych *J. Toboła & K. Kutorasiński*
- Rola efektów relatywistycznych w materiałach do konwersji termoelektrycznej i magnetokalorycznej; *J. Toboła*
- Obliczenia wpływu entropii na stabilność krystaliczną, strukturę elektronową i własności magnetyczne stopów wieloatomowych *J. Toboła*
- Struktura elektronowa i własności transportowe nowych materiałów na ogniwa jonowe; *J. Toboła*

Badanie struktury elektronowej i oddziaływania elektron-fonon w nadprzewodzących izolatorach topologicznych



Electron-phonon interaction: source of classical superconductivity

Important parameter: **electron-phonon coupling constant** λ 0.1 (Cu), ~1 (Nb), ~1.5 (Nb3Sn)

Critical temperature: McMillan's equation:

$$T_c = \frac{\omega_{log}}{1.20} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^\star(1+0.62\lambda)}\right]$$

μ* ~ 0.10 - 0.15

task: calculate λ

RMTA - *rigid muffin tin approximation*

$$\lambda_{ep} = \sum_i \frac{\eta_i}{M_i \langle \omega_i^2 \rangle}$$

η = response from electrons on atomic vibration

$$\eta_i = \sum_l \frac{(2l+2)n_l^i(E_F)n_{l+1}^i(E_F)}{(2l+1)(2l+3)N(E_F)} \left| \int_0^{R_{MT}^i} r^2 R_l^i(E_F,r) \frac{dV^i(r)}{dr} R_{l+1}^i(E_F,r) \right|^2$$

Electronic contribution

M <ω²> - lattice 'stiffness', phonon contribution

$$\langle \omega^2 \rangle = \int_0^{\omega_{max}} \omega F(\omega) d\omega \Big/ \int_0^{\omega_{max}} \frac{F(\omega)}{\omega} d\omega$$

F(ω) - phonon density of states

Implementacja nowych potencjałów wymienno-korelacyjnych w metodzie KKR-CPA dla układów złożonych

Density Functional Theory

How to approximate E_{XC} (LDA –local density approximation) ?

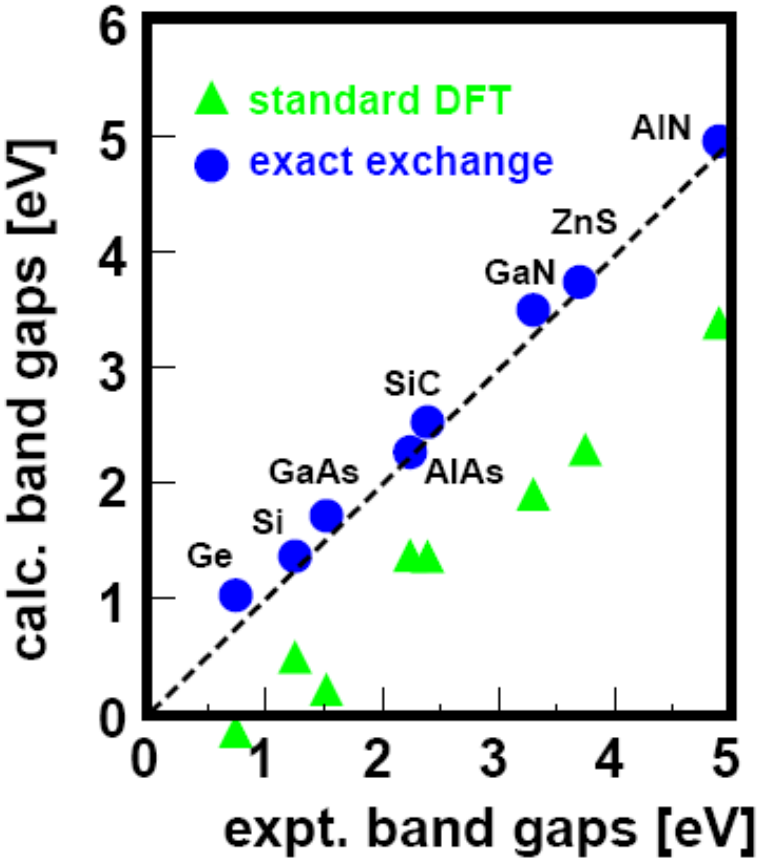
$$E_{xc}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}))$$

There are many analytical expressions for E_{xc}:
-Barth-Hedin, Vosko-Nusair, Lunqvist,
-Perdew-Wang, …(1970-80),
-Car-Parinello (QMC)

LSD –local spin density approximation

GGA –generalised gradient approx.

$$E_{xc}^{GGA}[n^{\uparrow}, n^{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n^{\uparrow}, n^{\downarrow}, \nabla n^{\uparrow}, \nabla n^{\downarrow})$$
$$\equiv \int d^3r n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xc}(n^{\uparrow}, n^{\downarrow}, \nabla n^{\uparrow}, \nabla n^{\downarrow}),$$



Thermoelectric properties

Carnot limit

search for optimum

Improvement of figure of merit

COOLING ELEMENTS

$COP = (T_H - T_C)(\gamma - 1)(T_C + \gamma T_H)^{-1}$

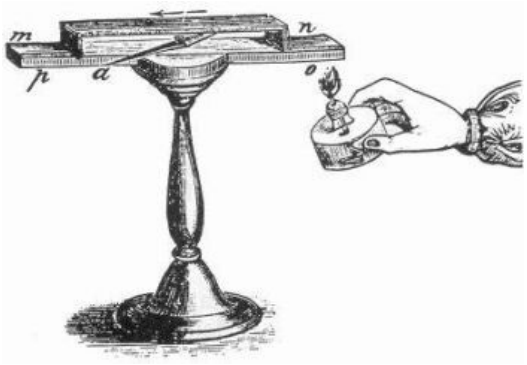
POWER GENERATORS

$\eta = (\gamma T_C - T_H)[(T_H - T_C + (\gamma + 1)]^{-1}$

Geometry of the devices

Physical properties of the system

$\gamma = (1+ZT)^{1/2}$



$$ZT = \frac{S^2\sigma}{\kappa}T = \underbrace{\frac{S^2}{L}}_{calculated}\frac{1}{1+\frac{\kappa_L}{\kappa_e}}$$

$$L \equiv \frac{\kappa_e}{T\sigma}$$

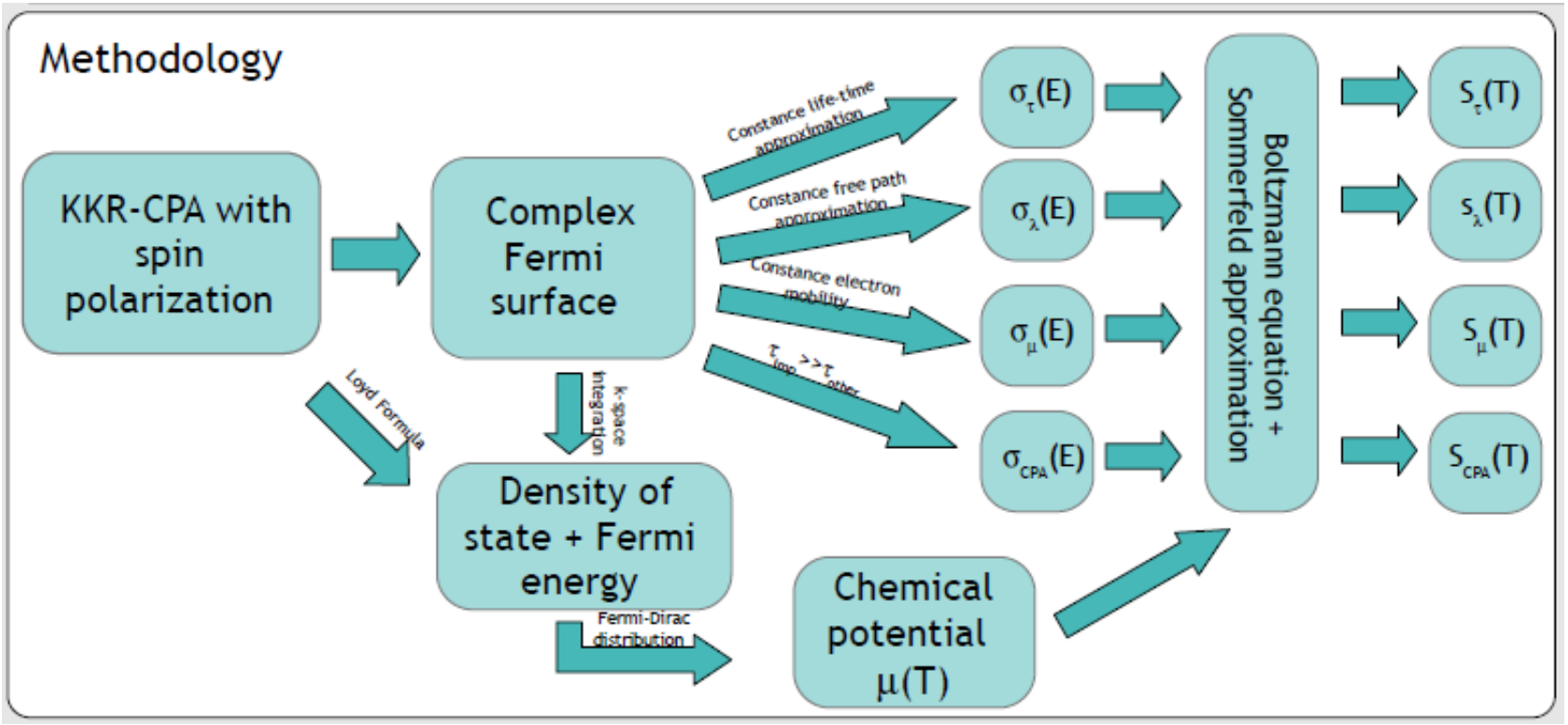
Lorentz factor

Thermal conductivity (phonons /electrons)

Teoretyczne poszukiwania nowych stopów termoelektrycznych i optymalizacja układów znanych

K. Kutorasinski (grant NCN, Sonata) **2 stypendia** 2000zł/mies. przez 3 lata (2015-2018); preferencje: 1 fizyk + 1 informatyk

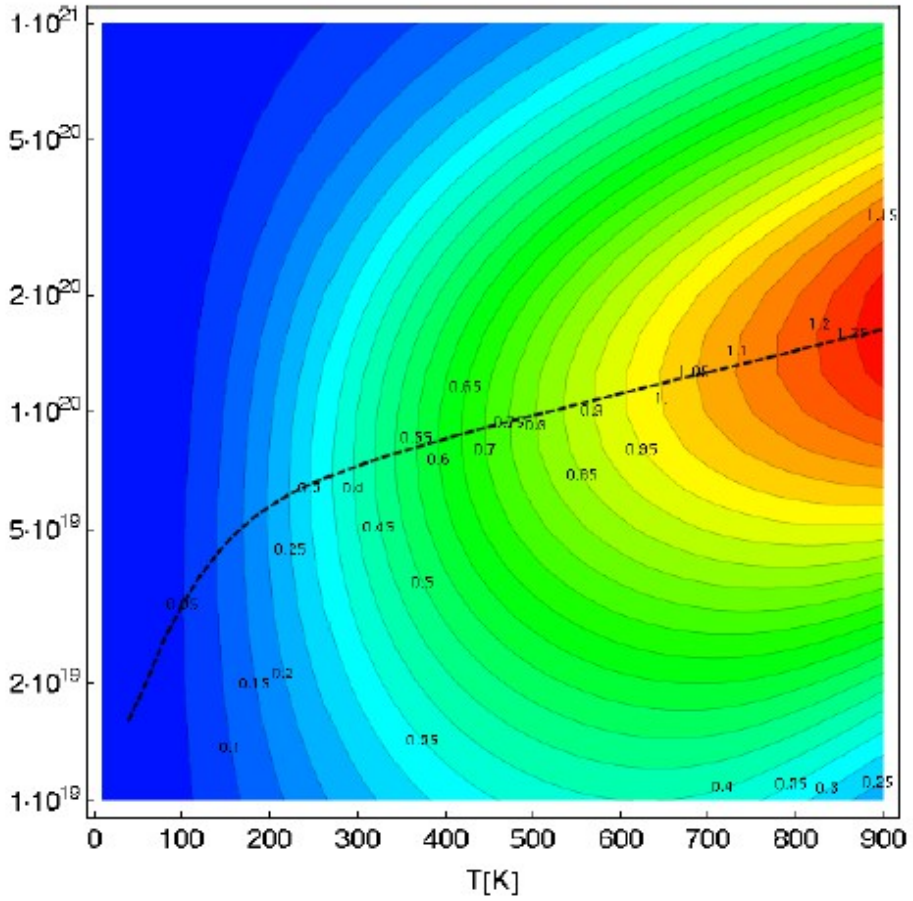
Boltzmann transport & KKR-CPA calculations



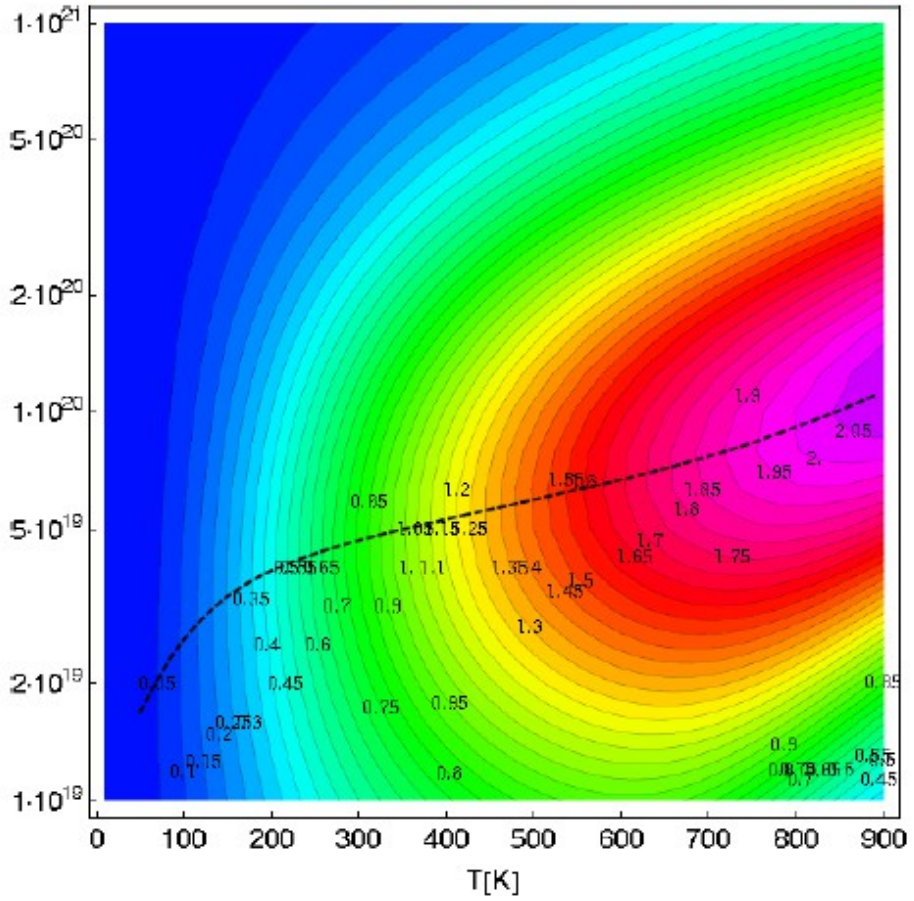
(1) τ = const; (2) λ = const; (3) μ = const; (4) CPA (velocity + life-time);

ZT *vs.* n/p & T

lattice thermal conductivity as parameter



$\kappa_l = 1.25$ W/mK



0.5 W/mK

Kutorasinski et al. (JT), Phys. Rev. B 87 (2013) 195205.

Full form of Dirac equation including four components

$$\left(\beta mc^2 + c(\alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3)\right)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

$$\begin{pmatrix} (mc^2 - E + e\phi) & c\sigma\cdot\left(p - \frac{e}{c}A\right) \\ -c\sigma\cdot\left(p - \frac{e}{c}A\right) & (mc^2 + E - e\phi) \end{pmatrix}\begin{pmatrix}\psi_+ \\ \psi_-\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix}$$

More readable: non-relativistic approach of Dirac equation

$$H = H_0 + H_{\text{kinetic}} + H_{\text{so}} + H_{\text{Darwinian}}$$

$$H_{so} = \frac{1}{2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\left(\frac{g_s}{2m_e^2c^2}\right)\frac{\vec{L}\cdot\vec{S}}{r^3}$$

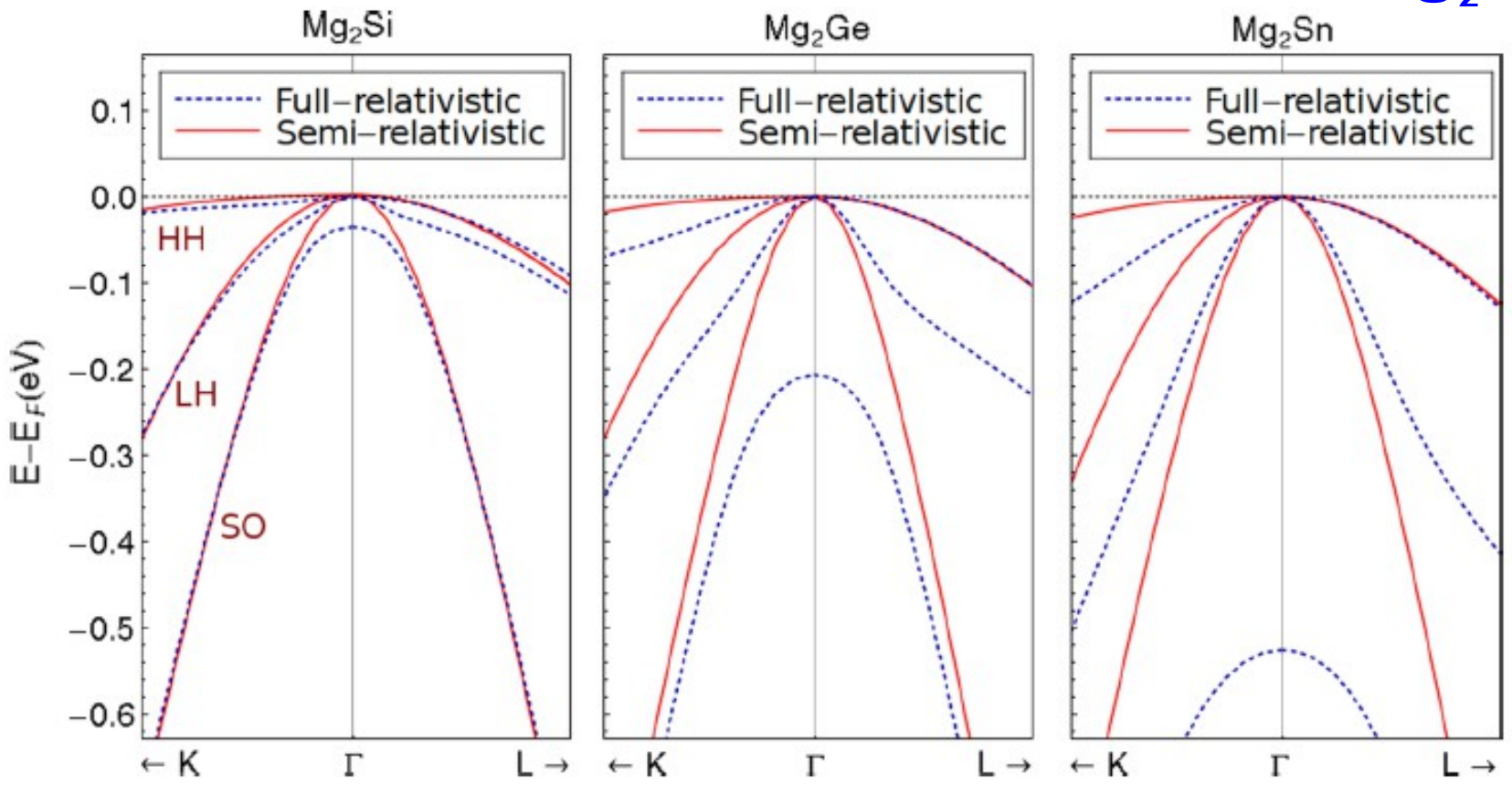
$$H_{\text{kinetic}} = -\frac{p^4}{8m^3c^2}$$

$$\langle H_{SO}\rangle = \frac{{E_n}^2}{m_e c^2}\left(n\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l\left(l+\frac{1}{2}\right)(l+1)}\right)$$

$$H_{\text{Darwinian}} = \frac{\hbar^2}{8m_e^2c^2}\,4\pi\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\delta^3(\vec{r})$$

SO splitting ~ $\dfrac{Z^4}{n^3(j+1/2)}10^{-5}$ eV

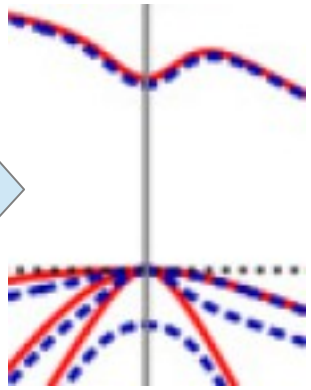
Effect of S-O on electronic bands in Mg_2X



X=	Si	Ge	Sn
Calculated (meV)	36	298	544
Measured (meV)	30[11]	200[11]	480[11],600[12]

[11] F. Vazquez, A. R. Forman, and M. Cardonna *Phys. Rev.*, vol. 176, p. 905, 1968

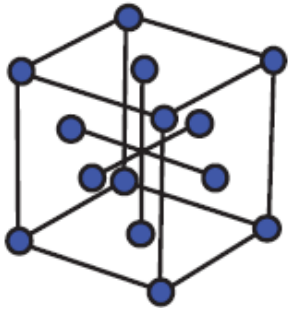
[12] L. A. Lott and D. W. Lynch, Phys. Rev. 141, 681 (1965)



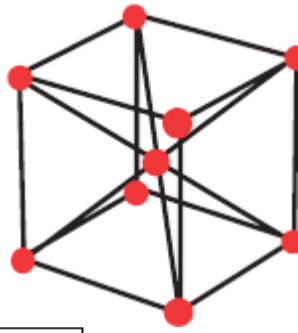
effect of S-O: on conduction bands - negligible

on valence bands – HUGE !

Obliczenia wpływu entropii na stabilność krystaliczną, strukturę elektronową i własności magnetyczne stopów wieloatomowych



$$F = E - TS$$



Many factors important:
- electronegativities of elements,
- VEC number of valence electrons
- atomic coordinations,
- symmetry of atoms sites,
- magnetic interactions,
- **degree of chemical disorder**

No. elements N	Configurational Entropy
2	0.693
3	1.098
4	1.386
5	1.609
6	1.791
7	1.945
8	2.079
10	2.302

NONG Zhi-sheng, et al/Trans. Nonferrous Met. Soc. China 22(2012) 1437−1444

FeTiCoNiVCrMnCuAl 系高熵合金中金属间化合物的第一性原理计算

农智升 [1,2]，朱景川 [1,2]，于海玲 [1]，来忠红 [1]

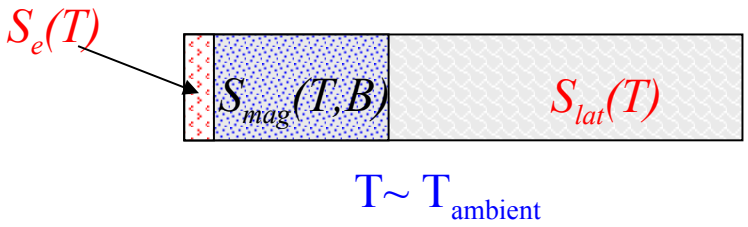
1. 哈尔滨工业大学 材料科学系，哈尔滨 150001；
2. 哈尔滨工业大学 金属精密热加工国家级重点实验室，哈尔滨 15000

$$S_{conf} = -k_B \sum_{i=1}^{N} c_i \ln c_i \quad \text{with} \quad \sum_{i=1}^{N} c_i = 1$$

High entropy alloys

$$S_{conf} = -k_B \sum_{i=1}^{N} 1/N \ln 1/N = k_B \ln N$$

Magnetocaloric effect & MC materials



Entropy

$$S_{tot} = S_{el} + S_{mag} + S_{lat}$$

$$\Delta S_{mag} \nearrow + \Delta S_{lat} \searrow = 0$$

Adiabatic Process

$$\Delta S_{mag}(T,\Delta B) = \int_0^B \left(\frac{\partial M}{\partial T}\right)_{\mathbf{B}} .dB$$

Calorific Capacity

$$C_p(B,T)$$

$$\Delta S_{lat} = C_p(B,T)\frac{\Delta T}{T}$$

Magnetic Entropy

$$\Delta S_{mag}$$

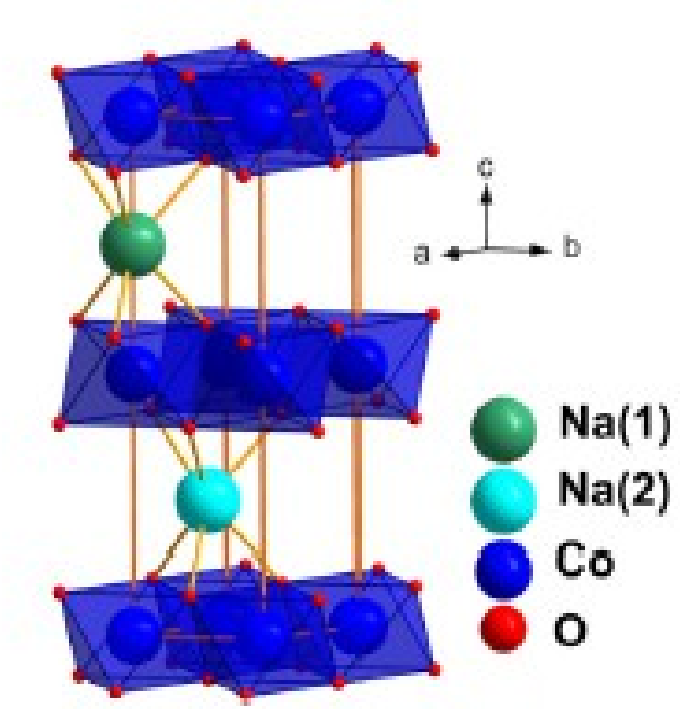
$$\Delta T_{max} = \frac{-T.\Delta S_{mag}}{C_p(B,T)}$$

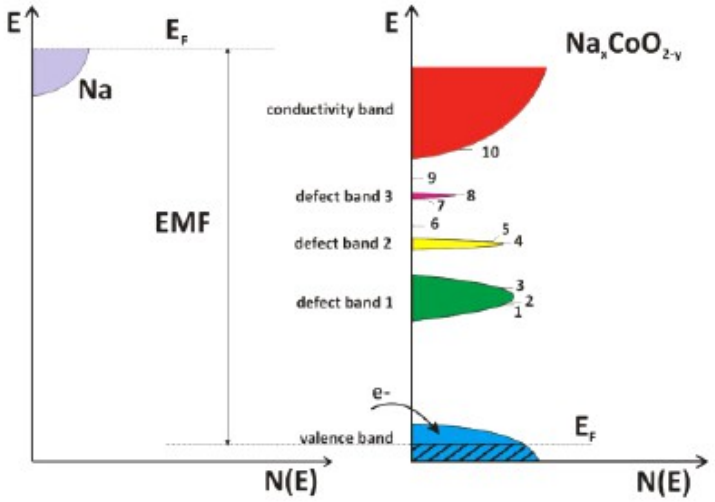
ΔT_{max}

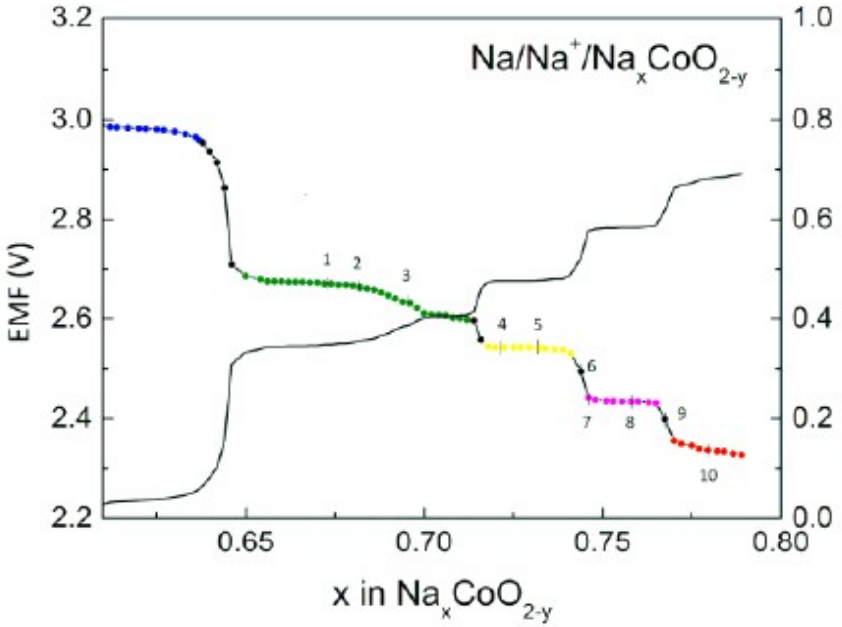
Struktura elektronowa i własności transportowe nowych materiałów na ogniwa jonowe

$$x\mathrm{Li}^+ + x\mathrm{e}^- + \mathrm{M}_a\mathrm{X}_b \leftrightarrow \mathrm{Li}_x\mathrm{M}_a\mathrm{X}_b,$$

$$x\mathrm{Na}^+ + x\mathrm{e}^- + \mathrm{M}_a\mathrm{X}_b \leftrightarrow \mathrm{Na}_x\mathrm{M}_a\mathrm{X}_b.$$







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