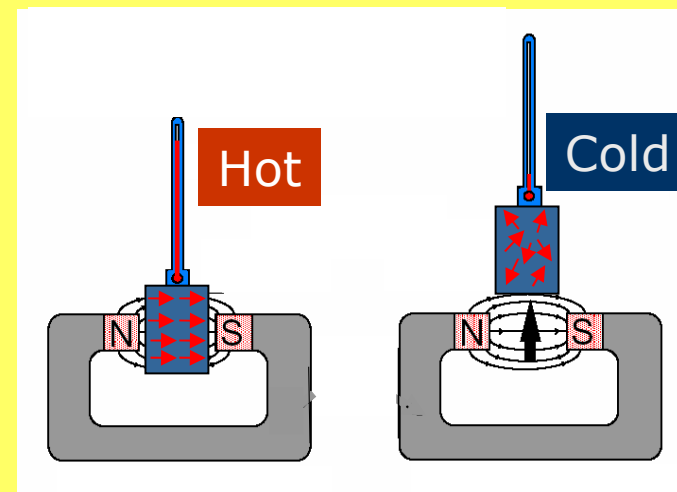


Seminarium WFIS, 11 maja 2007

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



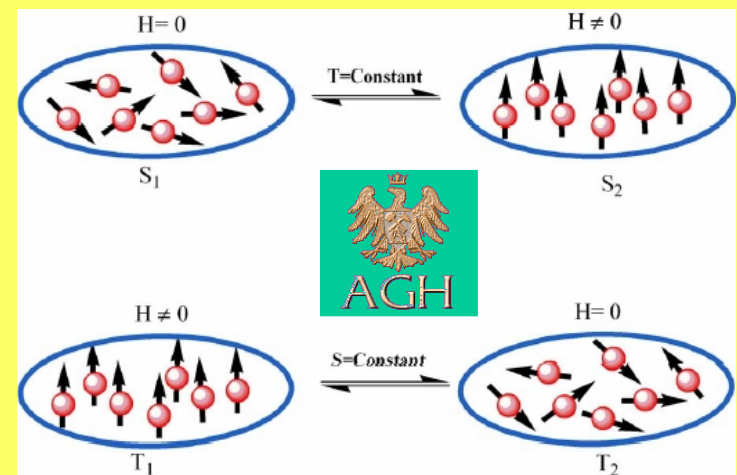
Chłodzenie niekonwencjonalne

czyli

gigantyczny efekt magnetokaloryczny i termoelektryczny w temperaturach pokojowych

Janusz Tobała

Katedra Fizyki Materii Skondensowanej
Wydział Fizyki i Informatyki Stosowanej, AGH



Efekt magnetokaloryczny : MCE

- trochę historii,
- analogia do cyklu termodyn.,
- wkłady do entropii,
- gigantyczny MCE,
- interesujące materiały MCE.
- **czy można naprawdę chłodzić ?**

Co można podpowiedzieć od strony teorii materii skondensowanej (np. jak zasymulować stan paramagnetyczny, gdzie szukać G-MCE, etc.)

a czego lepiej nie mówić

Efekt termoelektryczny : TE

- też trochę historii,
- „czworobok” termoelektryczny,
- wydajność zjawisk TE,
- interesujące materiały TE i koncepcje,

Co jesteśmy w stanie policzyć w układach termoelektrycznych - jak szukać efektywnych TE (domieszkowane półprzewodniki).

Podsumowanie + kolaboracja

Historia MCE

(1881) E. Warburg, żelazo grzeje się po włożeniu do pola magnetycznego $\sim 0.5-2$ K/1T, *Ann. Phys.*

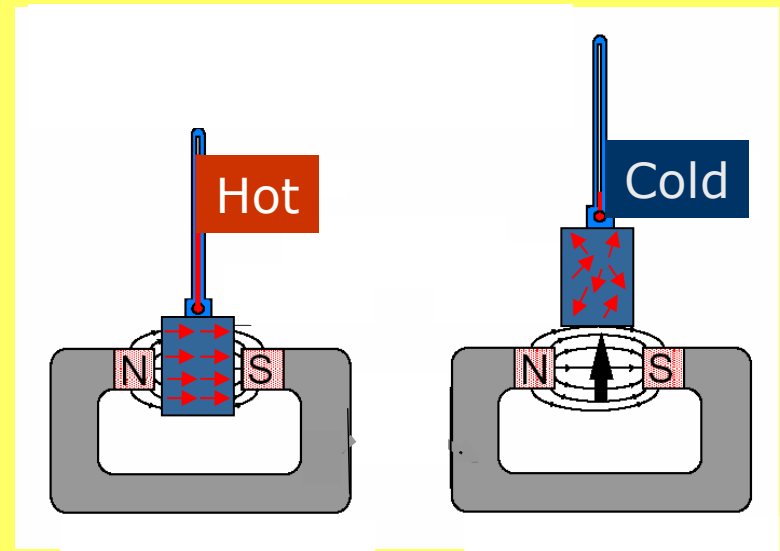
(1926) P. Debye (Nobel 1936, chemia)

(1927) W. Giauque (Nobel 1949, chemia)

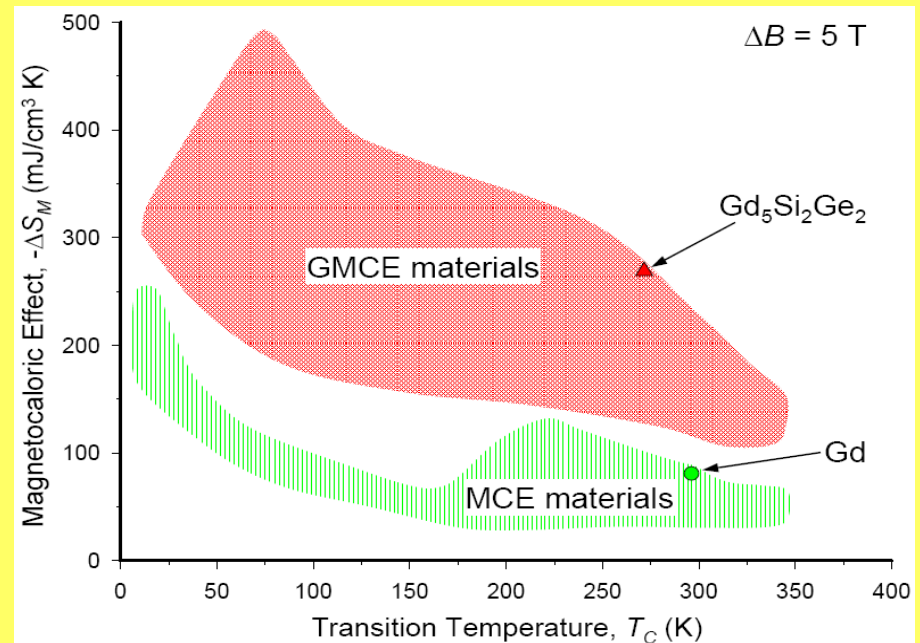
wyjaśniają efekt poprzez (roz)magnesowanie adiabatyczne - porządek/nieporządek momentów magnetycznych w (bez) B bez wymiany Q

(1997) Odkrycie gigantycznego efektu MCE
K. A. Gschneider & V. Pecharsky
(Ames Lab., USA), PRL (1997)

Efekt magnetokaloryczny jest cechą właściwą magnetycznych ciał stałych; jest największy w pobliżu temperatury przejścia w stan nieuporządkowany magnetycznie

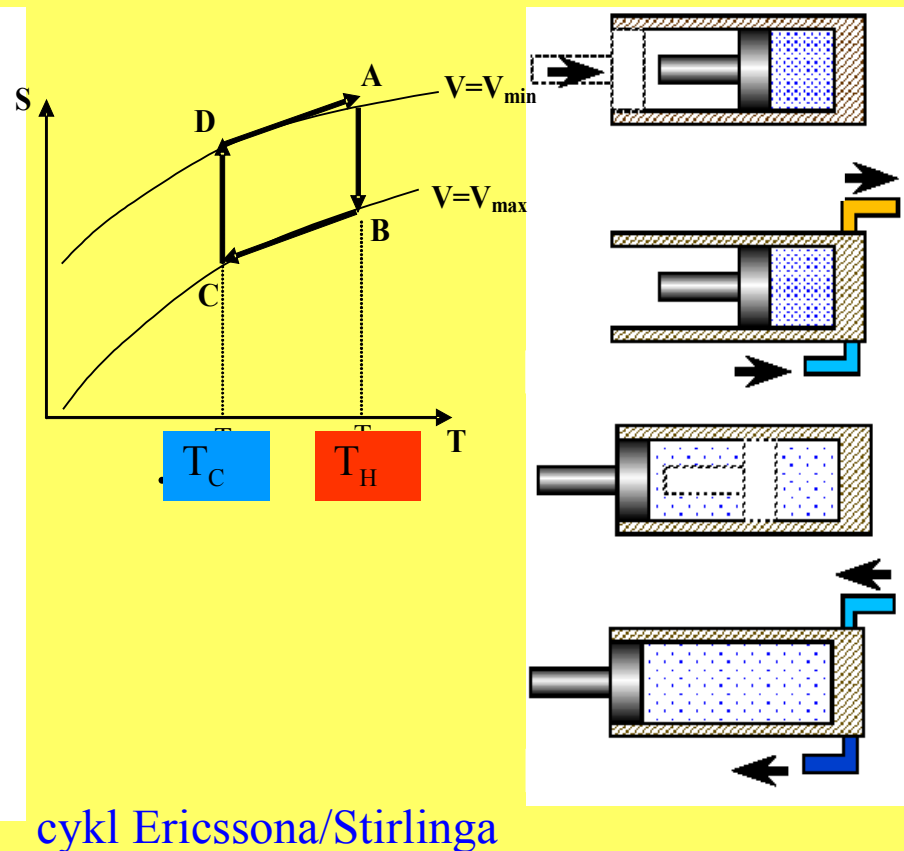
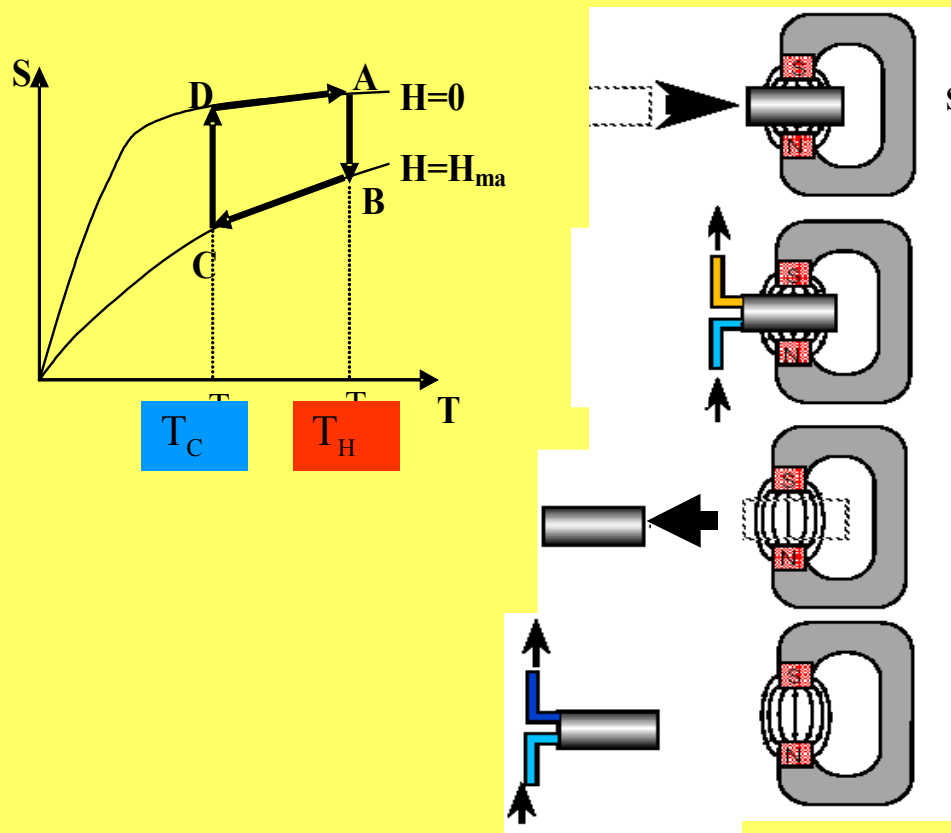


Adiabatyczne magnesowanie / rozmagnesowanie



Analogia (klasyczny cykl termodyn.)

Cykl magnesowanie/rozagnesowanie



W cyklu idealnym Carnot:

$$\eta = \frac{\Delta W}{\Delta Q_H} = 1 - \frac{T_C}{T_H}$$

$$\Delta W = \oint P dV = (T_H - T_C)(S_B - S_A)$$

$$\Delta Q_C = T_C(S_B - S_A)$$

$$\Delta Q_H = T_H(S_B - S_A)$$

Gdzie można spodziewać się MCE ?

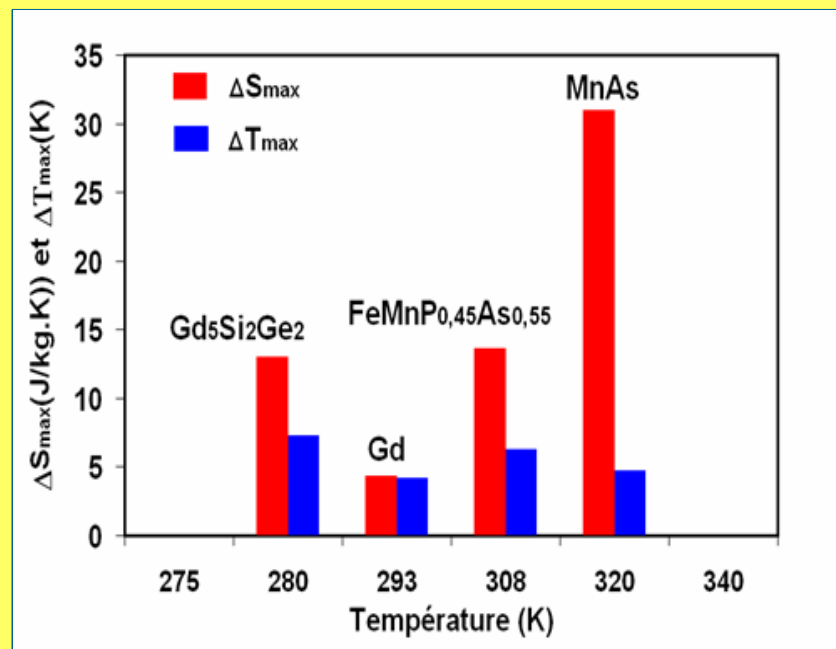
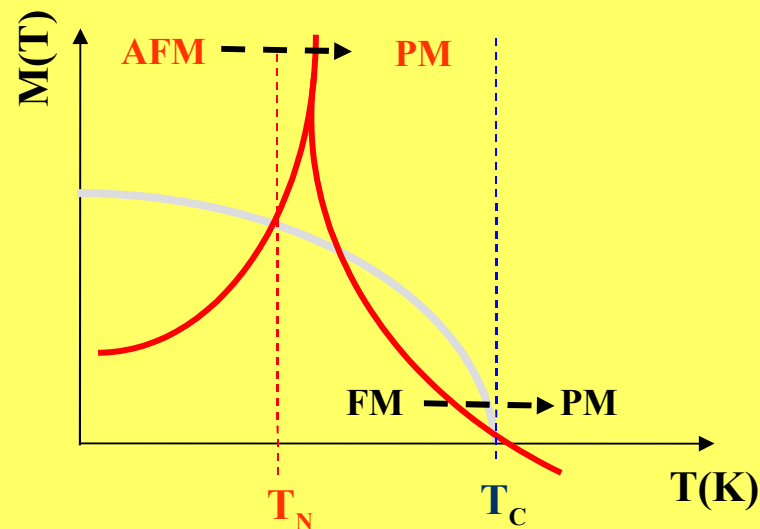
Rodzaje przejść fazowych (I & II):

FM-PM,
AFM-PM,
AFM-FM (ale mniejszy efekt !)

Rodzaje materiałów:

Ferromagnetyki, ferrimagnetyki,
antyferromagnetyki, ferromagnetyki
niejednorodne, amorficzne,
superparamagnetyki,

Najsilniejszy efekt w układach z
przejściem magneto-strukturalnym np.
MnAs, Gd(Si-Ge), La-Fe-Si, MnFe(As-P)



Parametry magnetokaloryczne układu

ΔT_S (ΔT_{ad}) - zmiana temperatury w procesie adiabatycznym (parametr intensywny)

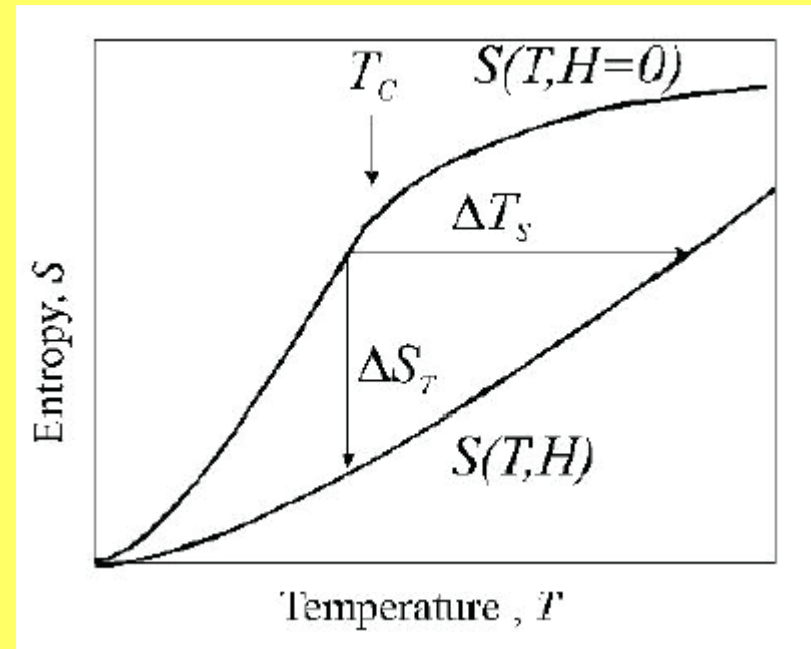
ΔS_T - zmiana entropii w procesie izotermicznym (parametr ekstensywny)

$$\boxed{\Delta T_S} = (T(S)_{H_2} - T(S)_{H_1})$$

$$\boxed{\Delta S_T} = S(T)_{H_2} - S(T)_{H_1} = \int_0^T \frac{C(T)_{p,H_2} - C(T)_{p,H_1}}{T} dT$$

$$\boxed{\Delta S_T} = \int_0^H \left(\frac{\partial M(T, H)}{\partial T} \right)_{p,H} dH$$

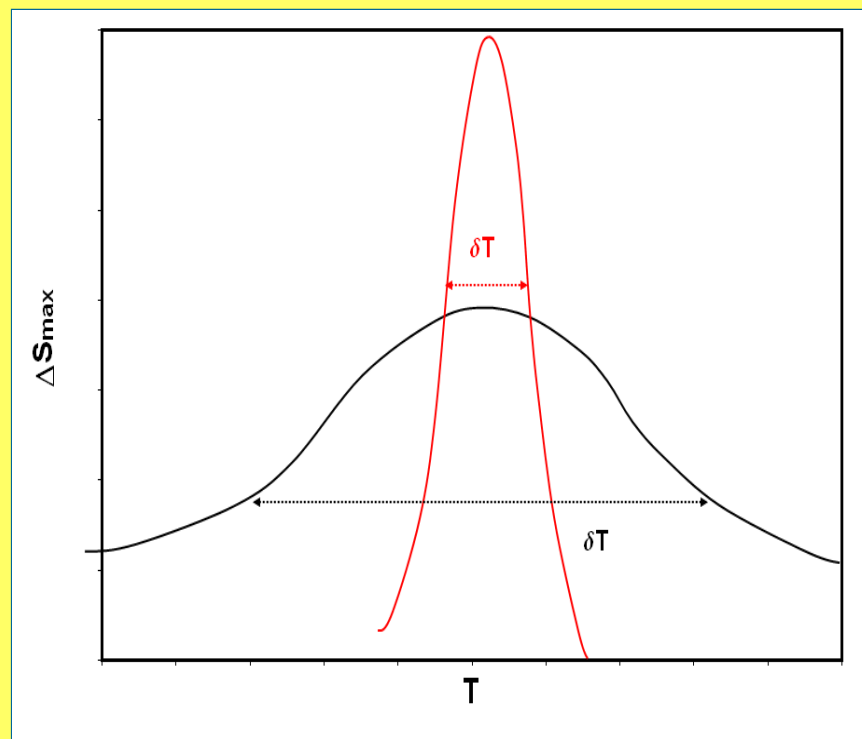
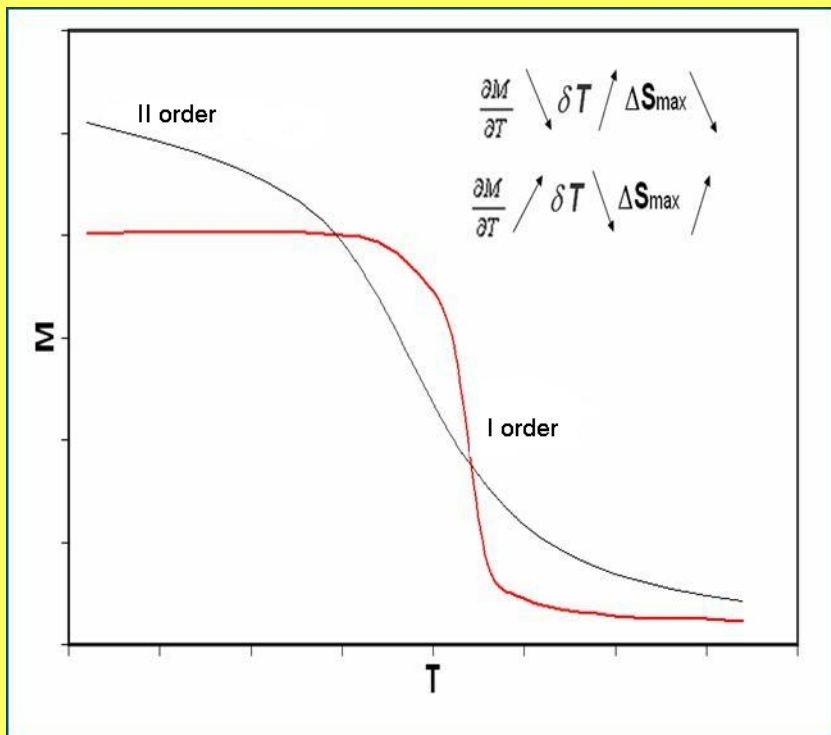
$$\boxed{\Delta T_S} = \int_0^H \left(\frac{T}{C(T, H)} \times \frac{\partial M(T, H)}{\partial T} \right)_{p,H} dH$$



Relacja Maxwella

$$\left(\frac{\partial S(T, H)}{\partial H} \right)_{p,T} = \left(\frac{\partial M(T, H)}{\partial T} \right)_{p,H}$$

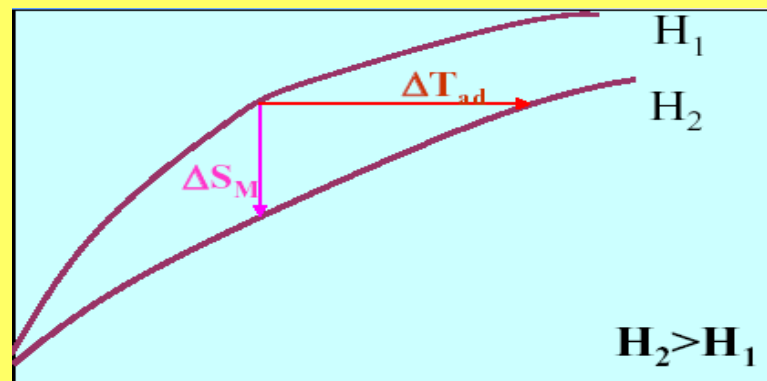
Warunki pojawienia się G-MCE



$$-RCP = \Delta S_M \Delta T_{ad} = B (M_1 - M_2)$$

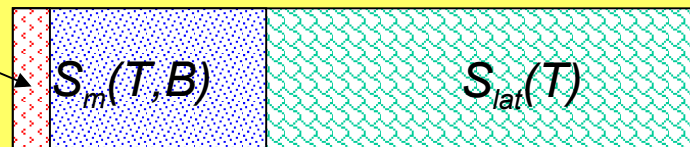
(relative cooling power)

- typ przejścia magnetycznego,
- uporządkowanie magnetyczne,
- własności magneto-elastyczne



Entropia (elektronowa, magnetyczna, sieciowa)

$$S_T = S_e + S_m + S_{lat}$$

 $S_e(T)$

 $T \sim T_{pokojo}$

$$\Delta S_m \uparrow + \Delta S_{lat} \downarrow = 0 \quad \text{proces adiabatyczny}$$

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

$$\Delta T_{\max} = \frac{-T \cdot \Delta S_m}{C_p(B, T)}$$

Pojemność cieplna

$$C_p(B, T)$$

Entropia magnetyczna

$$\Delta S_m$$

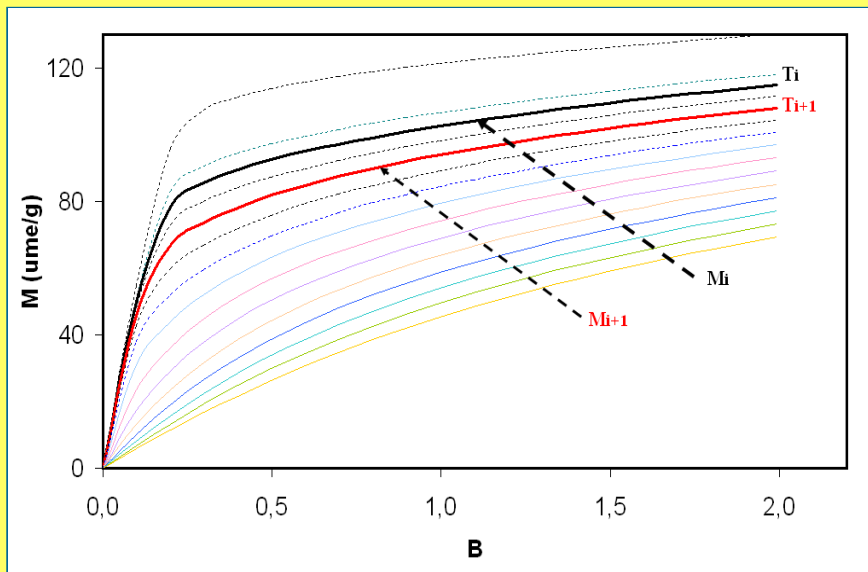
$$\Delta T_{\max}$$

Pomiary MCE

Krzywe magnetyzacji

$$\Delta S_m(T, \Delta B) = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B .dB \quad \text{oraz} \quad C_p(T, B)$$

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



Analiza danych

Magnetic measurements

$$M(T, B)$$

Correction of demagnetising field
($-N_d M$)

$$\Delta S_m = \sum_i \frac{1}{T_{i+1} - T_i} (M_i - M_{i+1}) \Delta H_i$$

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

Giant Magnetocaloric Effect in $Gd_5(Si_2Ge_2)$

V. K. Pecharsky and K. A. Gschneidner, Jr.

Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-3020

(Received 22 November 1996)

An extremely
a change in the
magnetocaloric
order [ferromag

Transition-metal-based magnetic refrigerants

hen subjected to
magnetic field)
is due to a first
the magnetic field

Itinerant-electron metamagnetic transition and large magnetocaloric effects
in $La(Fe_xSi_{1-x})_{13}$ compounds and their hydrides

Inverse magnetocaloric effect in
ferromagnetic Ni-Mn-Sn alloys

LETTERS

Ambient pressure colossal magnetocaloric
effect tuned by composition in $Mn_{1-x}Fe_xAs$

ARIANA DE CAMPOS¹, DANIEL L. ROCCO¹, ALEXANDRE MAGNUS G. CARVALHO¹, LUANA CARON¹,
ADELINO A. COELHO¹, SERGIO GAMA^{1*}, LUZELI M. DA SILVA¹, FLÁVIO C. G. GANDRA¹,
ADENILSON O. DOS SANTOS¹, LISANDRO P. CARDOSO¹, PEDRO J. VON RANKE² AND

manganites, RCo_2 Laves phases, La-Fe-Si

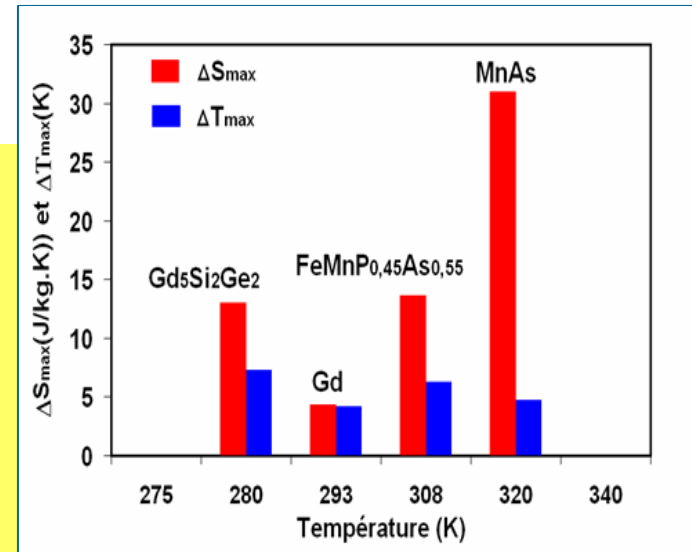
PRL **78**, 4494 (1997)

Nature **415**, 150 (2002)

PRB **67**, 104416 (2004)

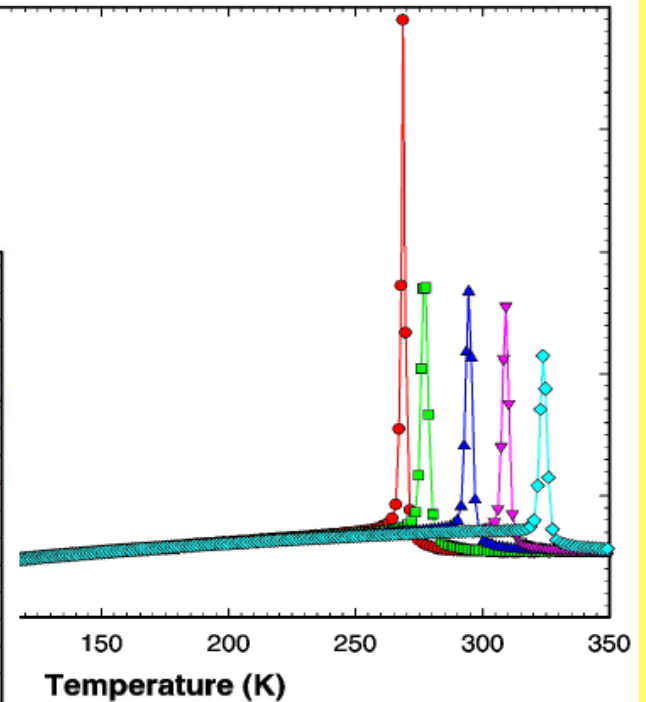
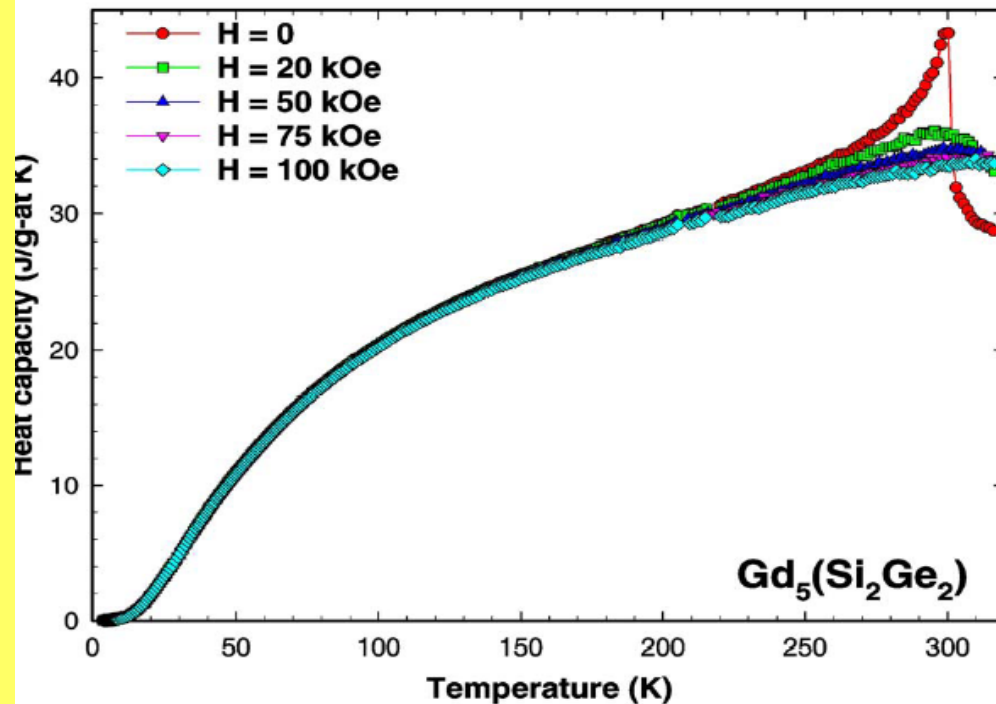
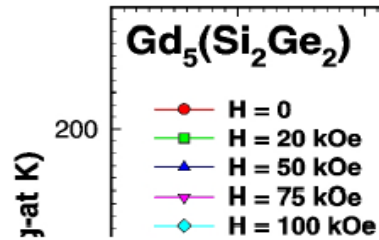
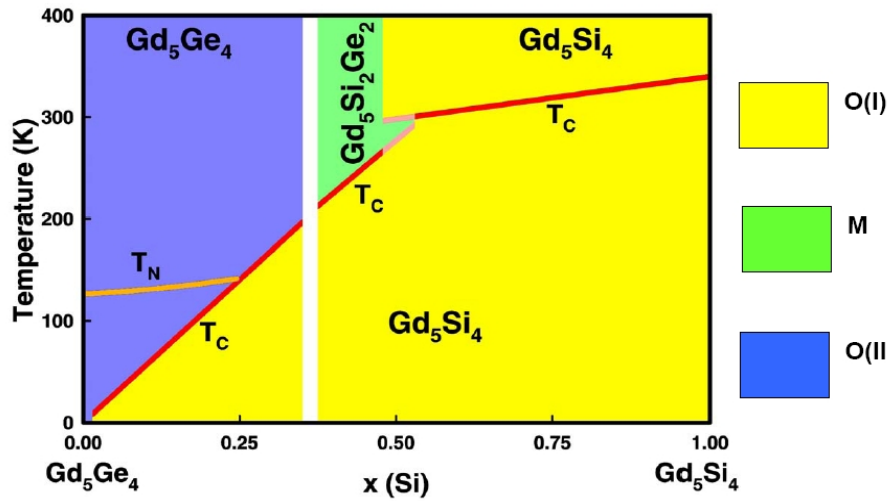
Nature Mat. **4**, 450 (2005)

Nature Mat. **5**, 803 (2006)

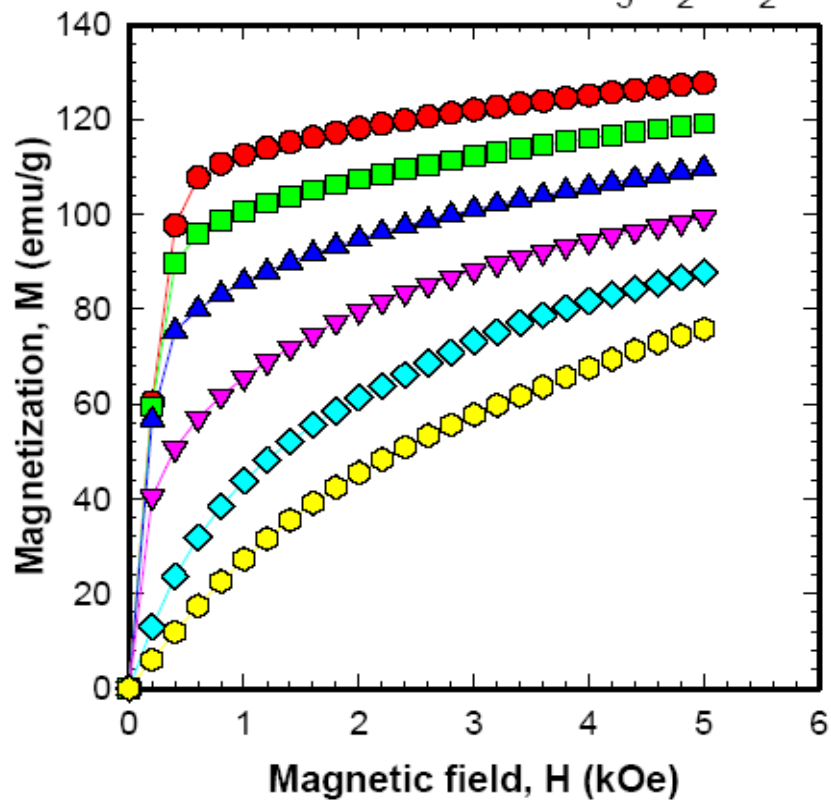


Układ G-MCE

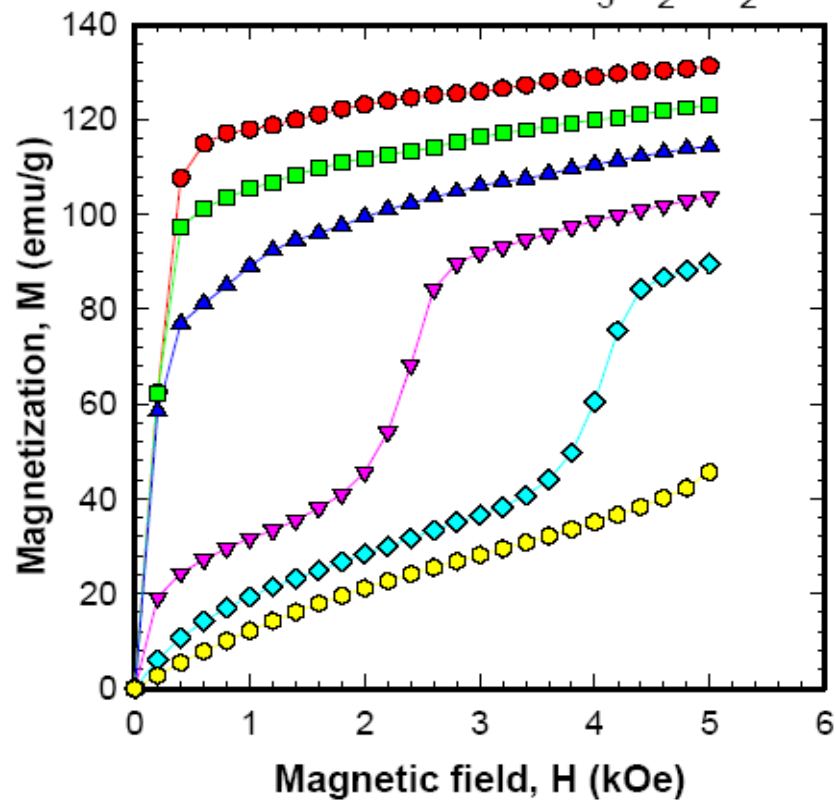
Pecharsky & Gschneider, 1997-2007

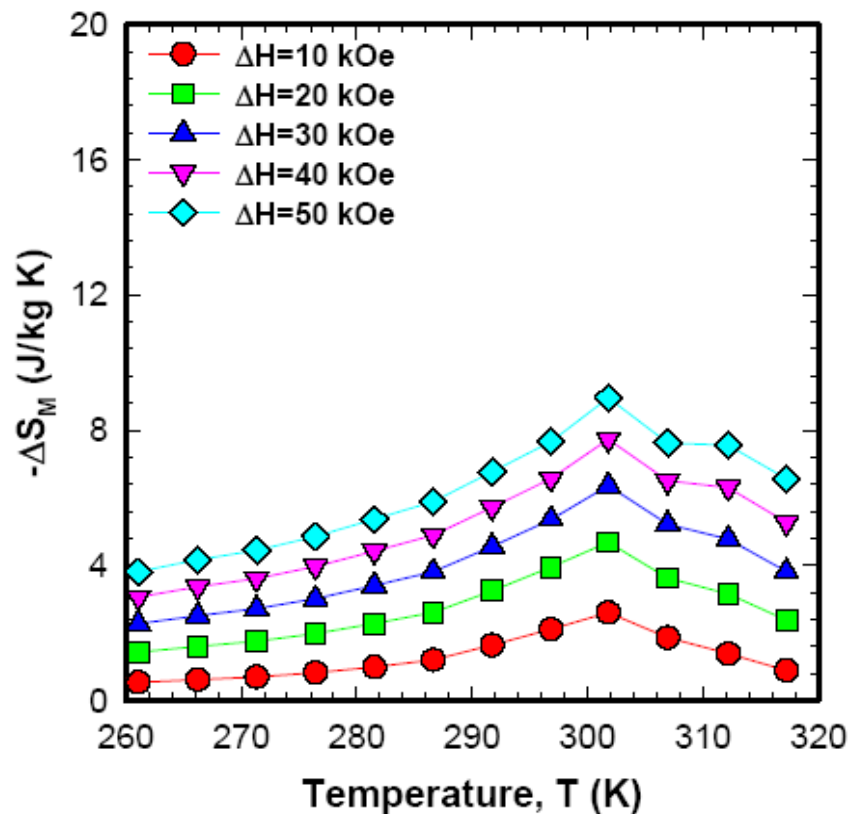
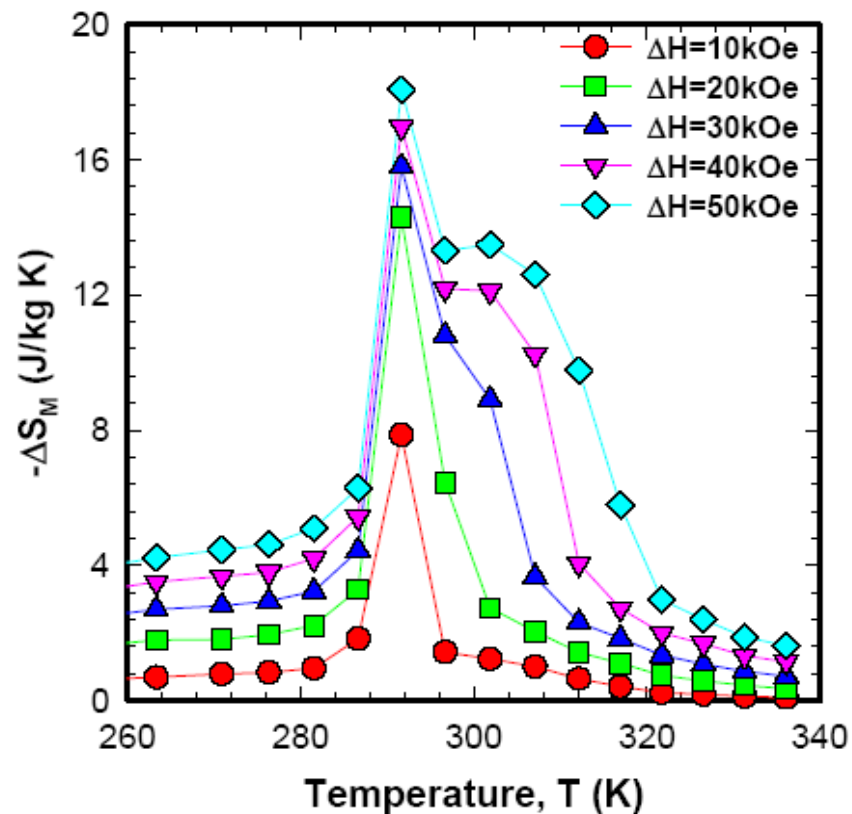


RT Orthorhombic $Gd_5Si_2Ge_2$

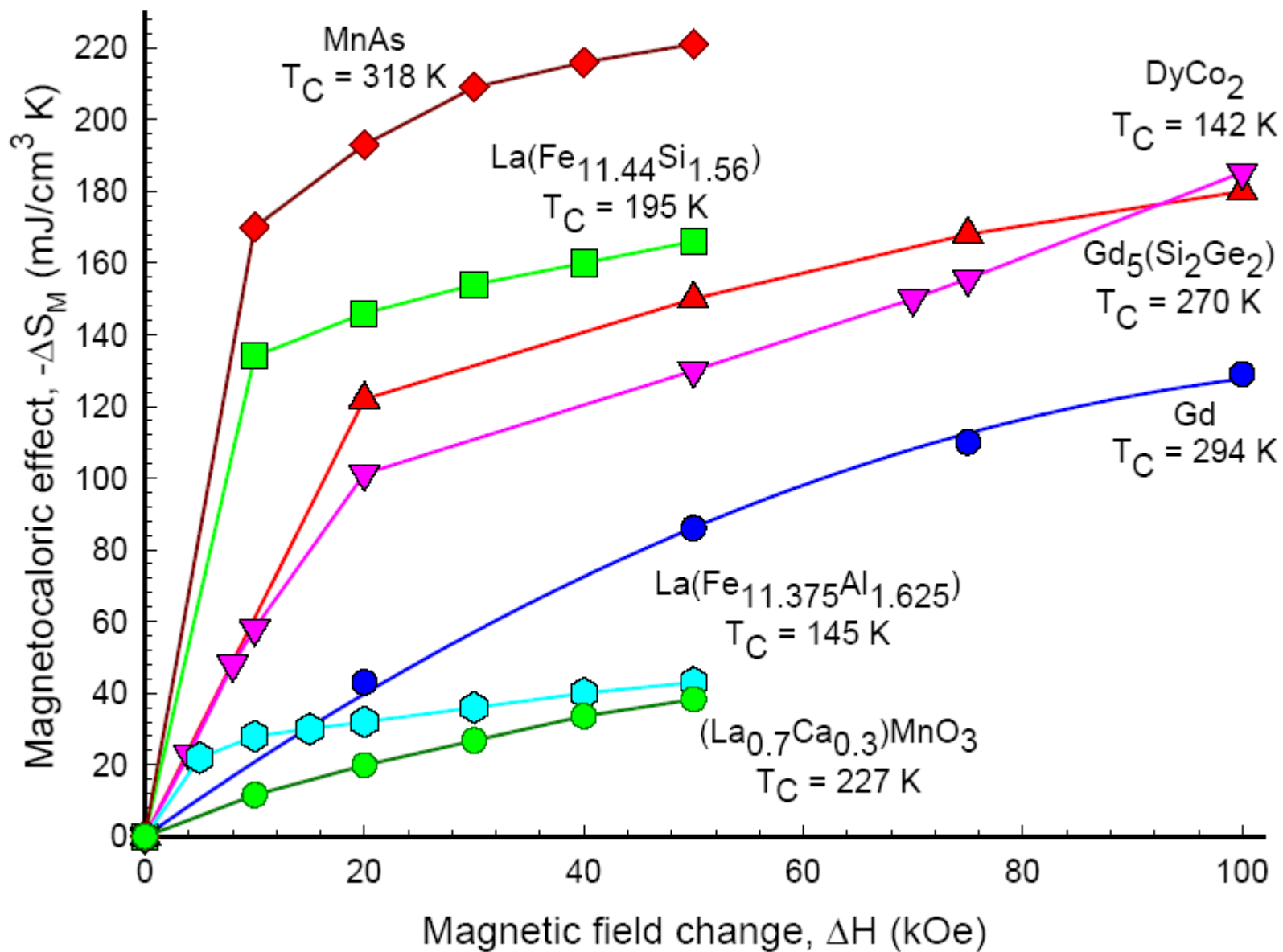


RT Monoclinic $Gd_5Si_2Ge_2$

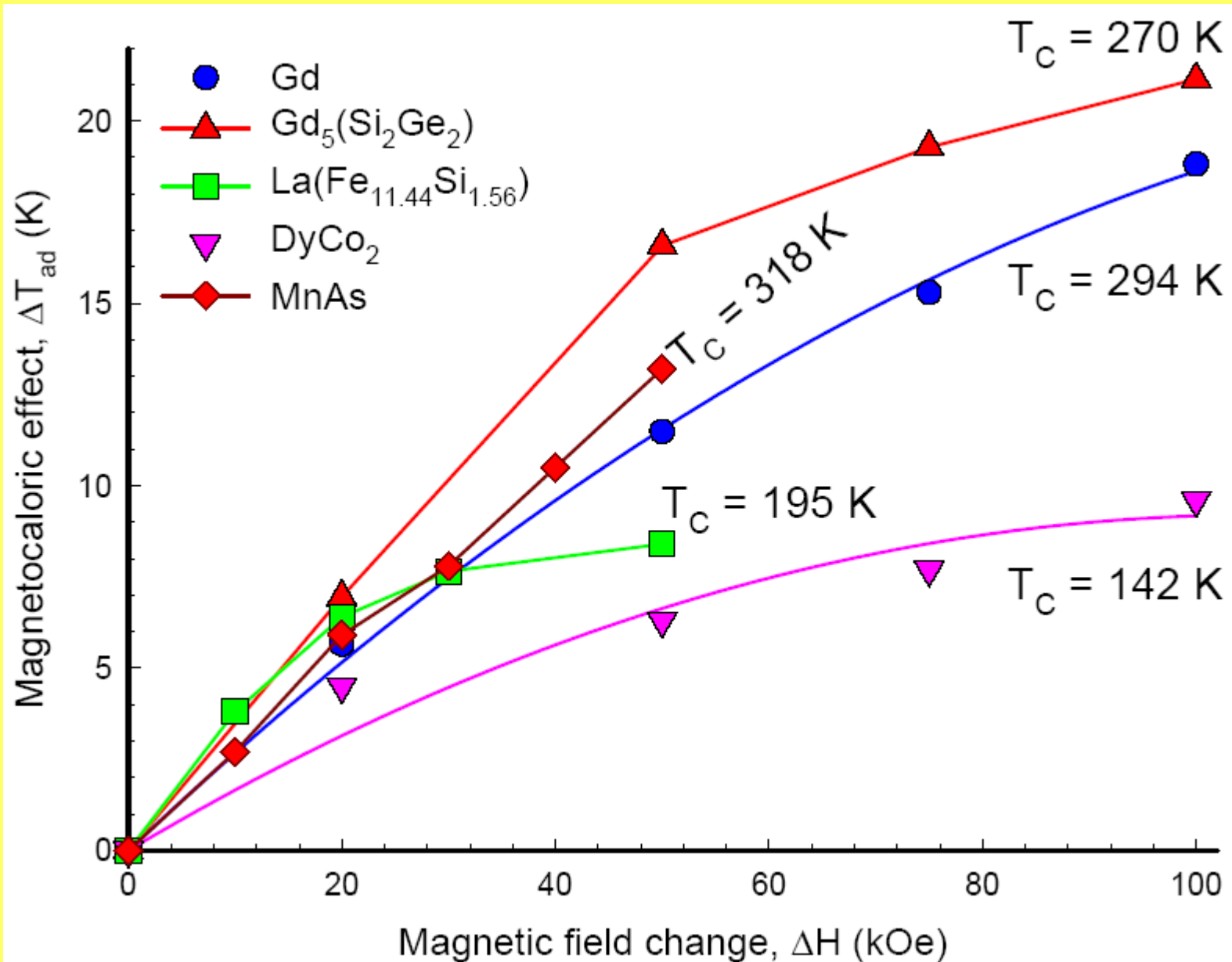


RT Orthorhombic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ RT Monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ 

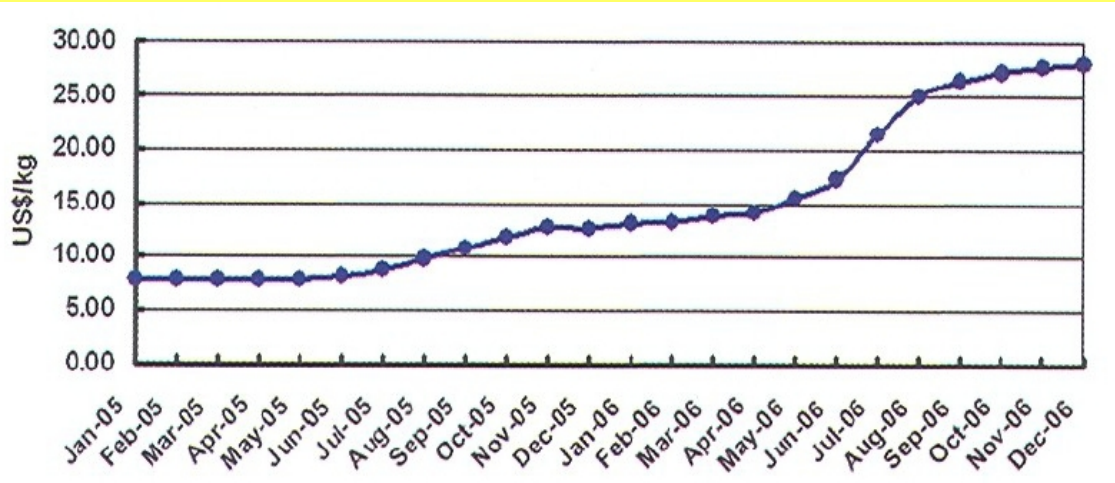
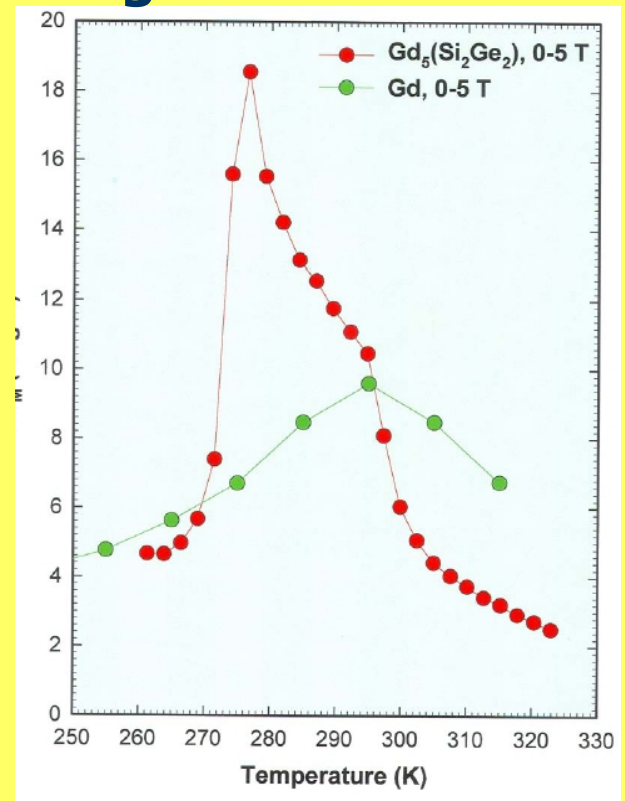
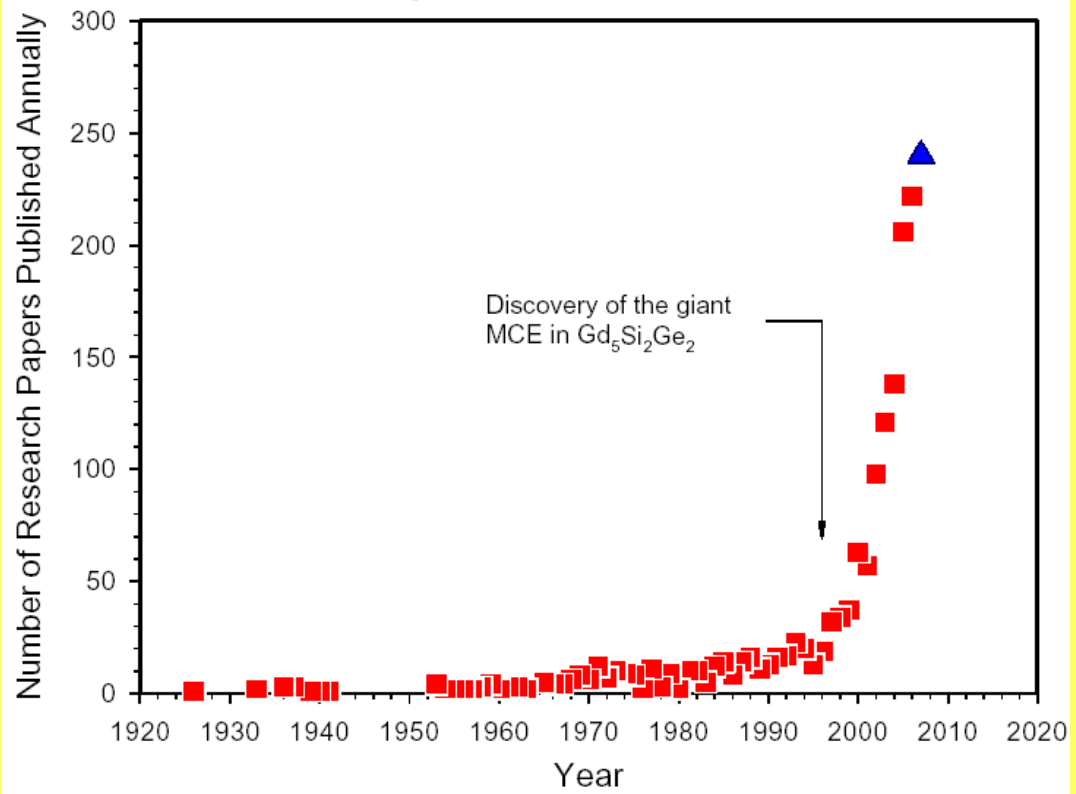
Nowe materiały MCE (skok entropii)



Nowe materiały MCE (skok temperatury)



Gigantyczny MCE – potrzeba magneśców



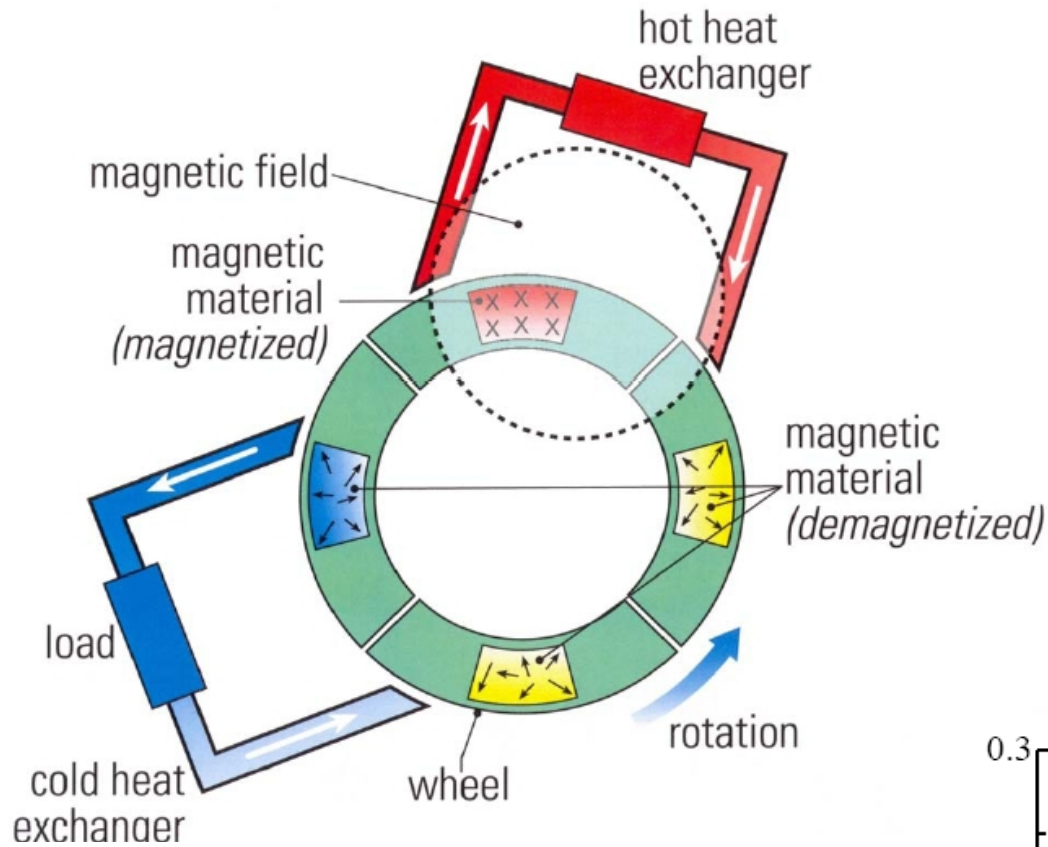
Active magnetic refrigerator (AMR), np. stopy Gd, La-Fe-Si

0.1-100 kg / AMR

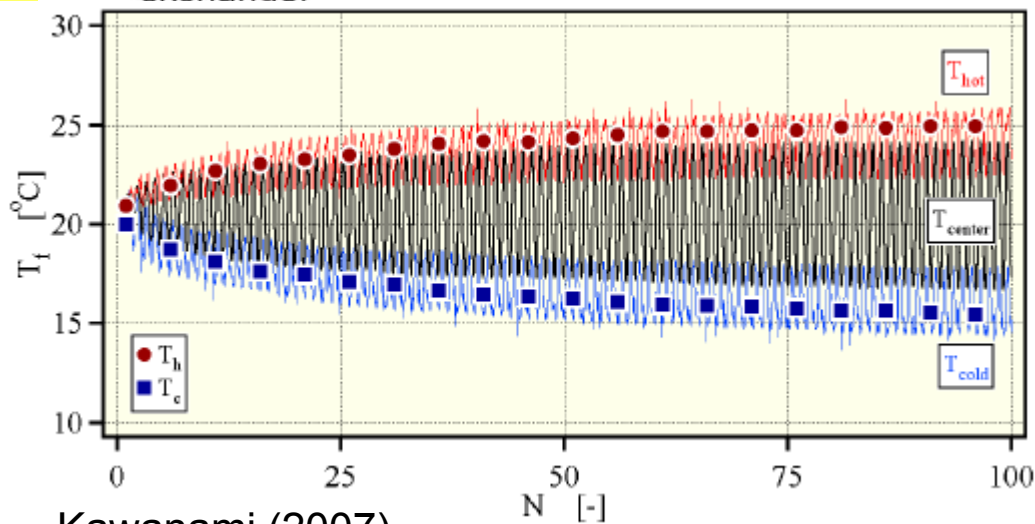
Źródła pola magnetycznego Nd-Fe-B

0.1-100 kg / AMR

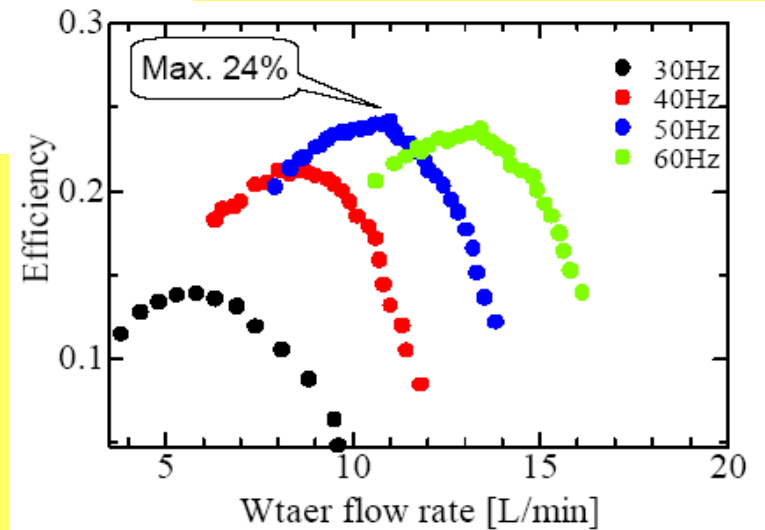
ASTRONAUTICS
rotary device (2001)



Okamura (2007)

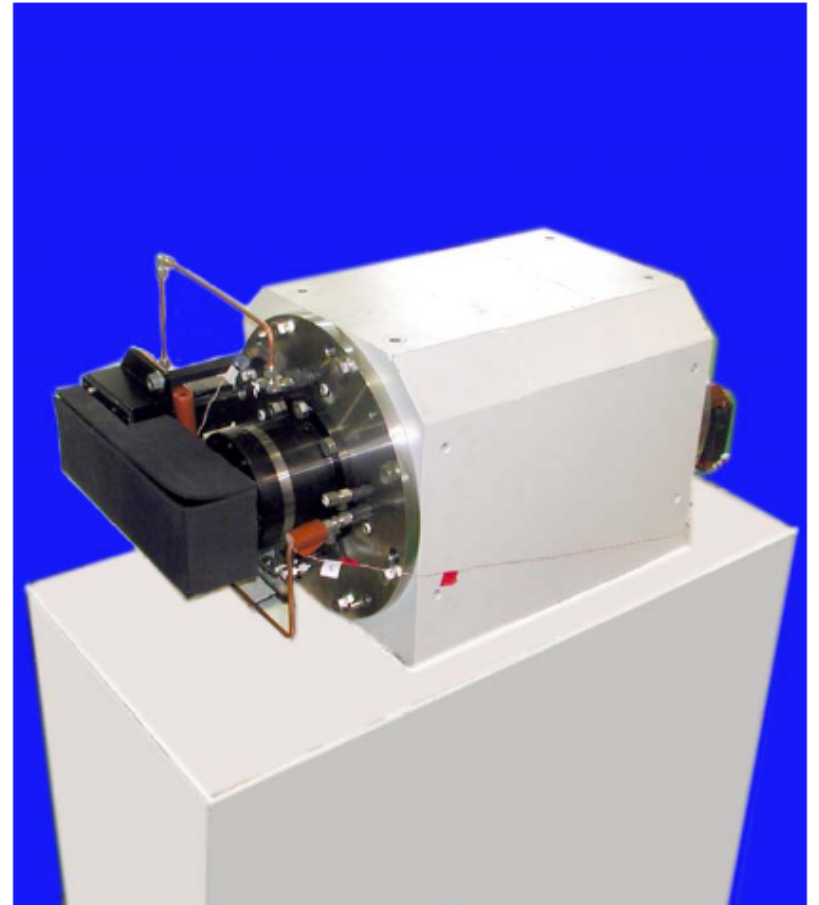
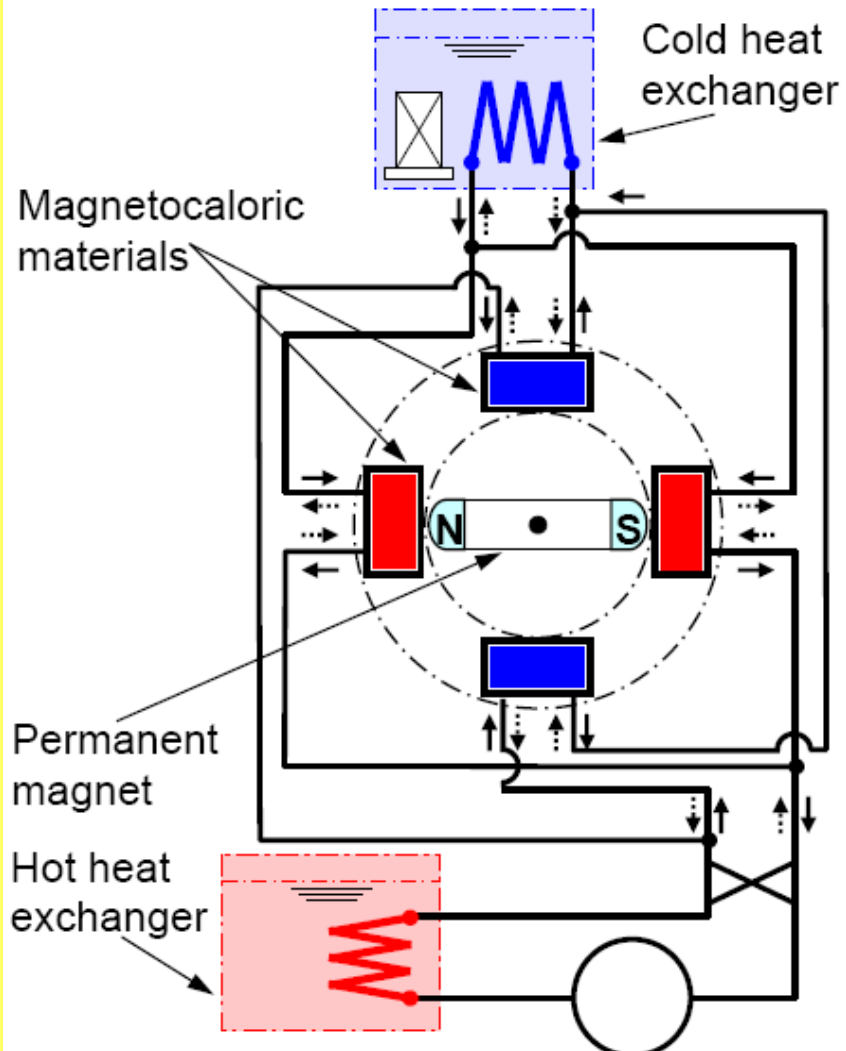


Kawanami (2007)



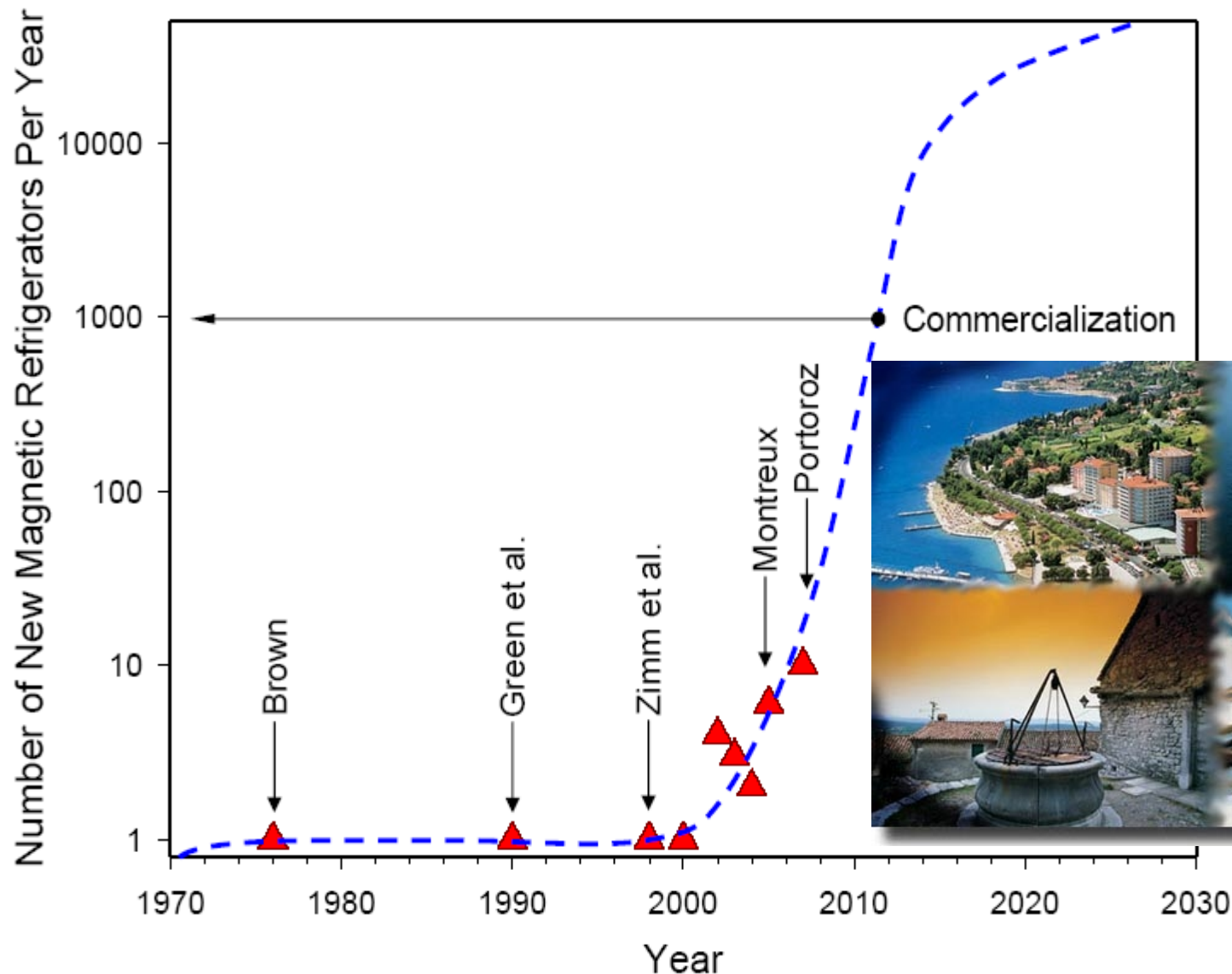
$$\text{Efficiency} = (\text{Pump work}) / (\text{Power consumption})$$

TOSHIBA rotary device (2004)



Magnetyczne lodówki w pobliżu temperatury pokojowej

(S-growth curve for new technologies)



2nd International Conference of the IIR on Magnetic Refrigeration at Room Temperature, Portoroz, 11-13 April, 2007

Name	Location	Announcement Date	Type	Max. Cooling Power (W)	Max ΔT (K)	Max. Magnetic Field ^b (T)	Regenerator Material	Ref.
Los Alamos Natl. Lab.	Los Alamos, New Mexico, USA	March 2002	Charging-discharging a coil, no moving parts	3	15	1.7(S)	Gd powdr.	Blumenfeld <i>et al.</i> (2002)
Univ. Quebec, Trois Rivieres	Trois Riveires, Quebec, Canada	Feb. 2004	Reciprocating	2	14	2.0(S)	Gd-R alloys ^c	Richard <i>et al.</i> (2004)
George Washington Univ.	Ashburn, Virginia, USA	June 2005	Reciprocating	?	5	2.0(P)	Gd powdr.	Shir <i>et al.</i> (2005)
Nanjing Univ.	Nanjing, China	Sept. 27, 2005	Reciprocating	40	25	1.4(P)	Gd powdr. Gd ₅ (Si,Ge) ₄ powdr.	Lu <i>et al.</i> (2005)
Tokyo Inst. Tech.	Yokohama, Japan	Sept. 27, 2005	Rotary	60	4	0.77(P)	Gd-R alloys ^c	Okamura <i>et al.</i> (2005)
Univ. Victoria	Victoria, Canada	Sept. 27, 2005	Reciprocating	?	50	2.0(S)	Gd-R alloys ^c	Rowe, <i>et al.</i> (2005)
Natl. Inst. Appl. Sci. ^d	Strasbourg, France	Sept. 27, 2005	Rotary	360	14	2.4(P)	Gd	Vasile, Müller (2005) ^d
Astronautics	Madison, Wisconsin, USA	Sept. 27, 2005	Rotary	50	25	1.5(P)	Gd, Gd alloys ^c La(Fe,Si) ₁₃ H	Zimm (2005)

Entropy contributions and relations to *ab initio* calculations

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

adiabatic process

for $h^{\text{ext}} = 0$, the intergral gives S_{el}

$$S_{\text{mag}}(T, h^{\text{ext}}) = R \left[\sum_{\sigma} \int_{-\infty}^{\mu} \ln(1 + e^{-\beta(\varepsilon - \mu)}) \rho_{\sigma}^{\text{el}}(\varepsilon) d\varepsilon + \frac{1}{kT} \sum_{\sigma} \int_{-\infty}^{\mu} (\varepsilon - \mu) \rho_{\sigma}^{\text{el}}(\varepsilon) f(\varepsilon) d\varepsilon \right]$$

de Oliveira, Eur. Phys. J. B (2004)

$$S_{\text{lat}} = R \left[- \int \ln(1 - e^{-\beta \hbar \tilde{\omega}}) \rho^{\text{ph}}(\tilde{\omega}) d\tilde{\omega} + \frac{1}{kT} \int \frac{\hbar \tilde{\omega}}{(e^{\beta \hbar \tilde{\omega}} - 1)} \rho^{\text{ph}}(\tilde{\omega}) d\tilde{\omega} \right]$$

Phonon DOS is needed to estimate lattice contribution

$$\Delta S_{\text{mag}} + \Delta S_{\text{lat}} = 0$$

$S_{\text{el}} \approx \gamma T$ often sufficient

in MCE systems smaller than S_{mag} , S_{lat}

$$S_{\text{lat}}(T, h^{\text{ext}}) = \left[-3R \ln \left(1 - \exp \left(-\frac{\tilde{\Theta}_D}{T} \right) \right) + 12R \left(\frac{T}{\tilde{\Theta}_D} \right)^3 \int_0^{\tilde{\Theta}_D/T} \frac{x^3}{\exp(x) - 1} dx \right]$$

BUT this can be approximatively done e.g. from Debye model

Precise estimations can be made for electronic and phonon structure if DOS is known. With Debye temperature S_{lat} estimation may give good result and allows to interpret ΔS jump observed experimentally.

Simulations of electronic structure above Curie temperature - DLM (disordered local moments)

1. Analogy with chemical alloy within the coherent potential approximation) CPA with **2 atoms on 1 site**.
2. **atom A - Fe^{up}** (iron with magnetic moment 'up')
atom B - Fe^{down} (iron with magnetic moment 'down')
3. **A** and **B** atoms occupy the same crystallographic site.
4. For concentration 50% the total magnetic moment per site and unit cell is zero, but the 'local' magnetic moments may be **non-zero**.
5. CPA medium is used to **randomly distribute the magnetic moments** among the sites (like in **paramagnetic state**)

KKR+CPA

$T_c = 1250 \text{ K}$

Experiment

$T_c = 1044 \text{ K}$

Ferromagnetic phase transitions in metals

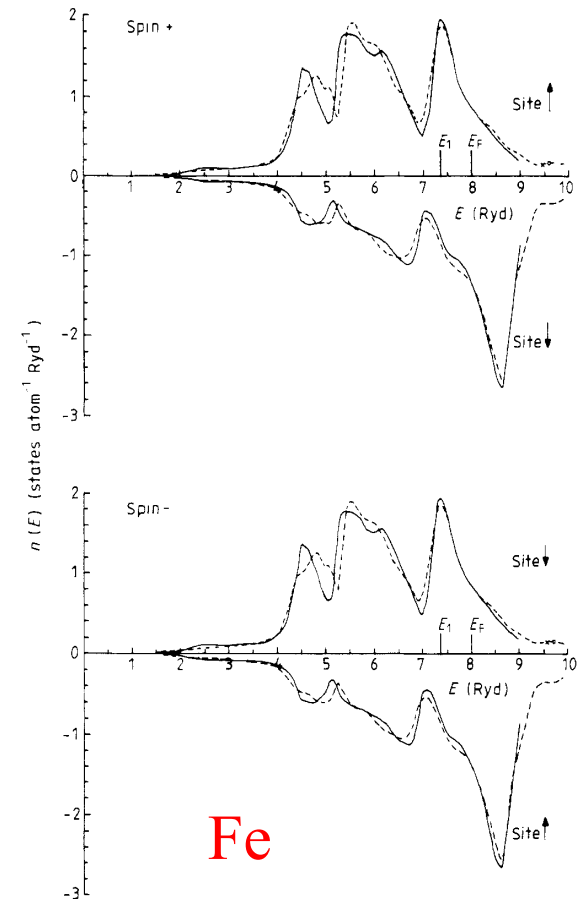


Figure 3. Density of states for Fe in its paramagnetic disordered local moment state.

Gyorffy et al., J. Phys. F (1985)

KKR-CPA method

Korringa-Kohn-Rostoker with coherent potential approximation

$$G(E) = \sum_{s=(+,-)} \sum_{k=1}^K \int_{V_k} d^3r \langle s, \mathbf{r} + \mathbf{a}_k | G(E) | s, \mathbf{r} + \mathbf{a}_k \rangle.$$

Bansil, Kaprzyk, Mijnaerends, Tobola,
Phys. Rev. B (1999) conventional KKR

Green function

Stopa, Kaprzyk, Tobola,
J.Phys.CM (2004)
novel formulation of KKR

$$\begin{aligned} & \langle s', \mathbf{r}' + \mathbf{a}_{k_{CP}} | G^{A(B)}(E) | s, \mathbf{r} + \mathbf{a}_{k_{CP}} \rangle \\ &= - \sum_{\sigma L} J_{\sigma L}^{A(B)}(s', \mathbf{r}') Z_{\sigma L}^{A(B)}(s\mathbf{r}) \\ &+ \sum_{\sigma' L', \sigma L} Z_{\sigma' L'}^{A(B)}(s', \mathbf{r}') T_{k_{CP}\sigma' L', k_{CP}\sigma L}^{A(B)} Z_{\sigma L}^{A(B)}(s\mathbf{r}) \end{aligned}$$

$$\begin{aligned} & \langle s', \mathbf{r}' + \mathbf{a}_{k'} | G(E) | s, \mathbf{r} + \mathbf{a}_k \rangle \\ &= - \sum_{\sigma L} J_{\sigma L}^{(k)}(s', \mathbf{r}') Z_{\sigma L}^{(k)}(s\mathbf{r}) \delta_{kk'} \\ &+ \sum_{\sigma' L', \sigma L} Z_{\sigma' L'}^{(k')} (s', \mathbf{r}') T_{k'\sigma' L', k\sigma L}^{CP} Z_{\sigma L}^{(k)}(s\mathbf{r}) \end{aligned}$$

$$\begin{aligned} G(E) = & - \frac{d}{dE} \left\{ \frac{1}{N} \sum_{\mathbf{k} \in BZ} \text{Tr} \ln [G_0^{-1}(E, \mathbf{k}) + D^{(j)} - D_{CP}]^{-1} \right\} \\ & - \frac{d}{dE} \{ c_A \text{Tr} \ln [\Psi_A^{-1} G^A] + c_B \text{Tr} \ln [\Psi_B^{-1} G^B] \\ & - \text{Tr} \ln G^{CP} \} + \frac{d}{dE} \left\{ \sum_{k \neq k_{CP}} \text{Tr} \ln [\Psi^{(k)}] \right\}, \quad (2.22) \end{aligned}$$

$$T_{k'\sigma' L', k\sigma L}^{CP} = \frac{1}{N} \sum_{\mathbf{k} \in BZ} [\tau_{CP}^{-1} - B(E, \mathbf{k})]_{k'\sigma' L', k\sigma L}^{-1}$$

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

Density of states $N(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^E dE' G(E')$

Lloyd formula

Kaprzyk et al. Phys. Rev. B (1990)

Fermi energy

$$N(E_F) = Z$$

Ground state properties

KKR-CPA code

Total density of states DOS

$$N(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^E dE G(E)$$

Component, partial DOS

$$\rho_{\sigma}(E) = \frac{\partial}{\partial E} N_{\sigma}(E).$$

Total magnetic moment

$$\mu = N_{+}(E_F) - N_{-}(E_F)$$

Spin and charge densities

$$\rho_{\sigma}^{(k)}(\mathbf{r}) = -\frac{1}{\pi} \int_{-\infty}^{E_F} dE \langle \sigma, \mathbf{r} + \mathbf{a}_k | G(E) | \sigma, \mathbf{r} + \mathbf{a}_k \rangle$$

Local magnetic moments

$$\mu^{(k)} = \mu_B \int_{\Omega_k} d^3r S^{(k)}(\mathbf{r})$$

Fermi contact hyperfine field

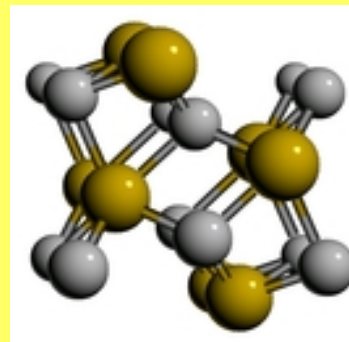
$$H_{Fermi} = \frac{8}{3} \pi \mu_B [\rho_{\uparrow}(0) - \rho_{\downarrow}(0)]$$

Bands $E(\mathbf{k})$, total energy, electron-phonon coupling, magnetic structures, transport properties, photoemission spectra, Compton profiles, ...

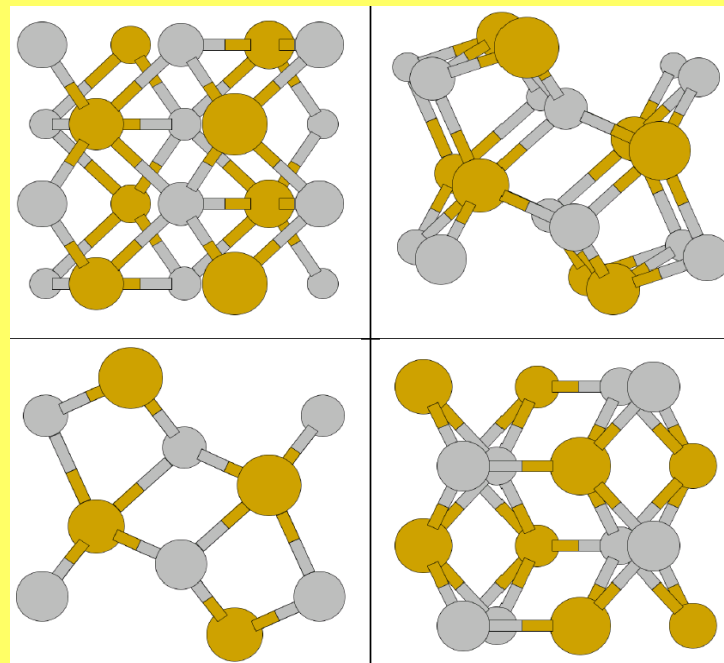
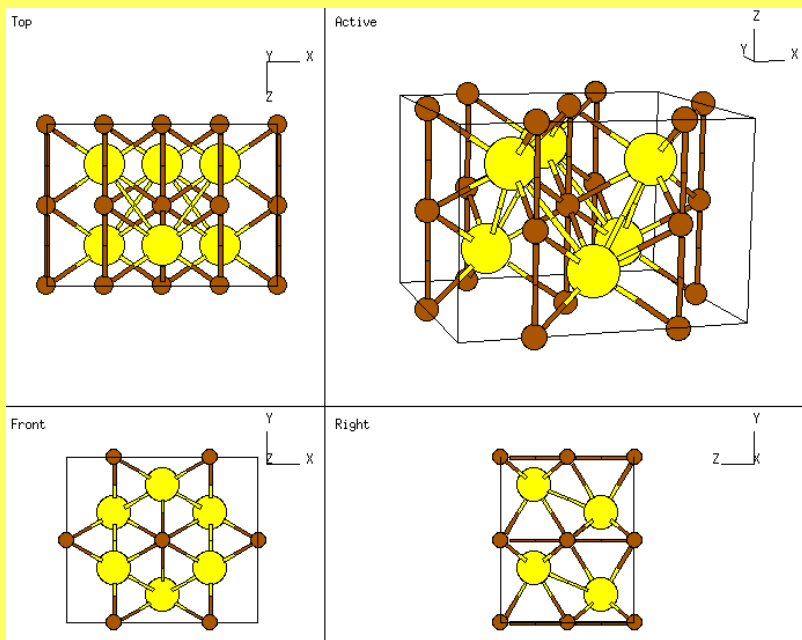
MnAs (magneto-structural transition) at 318 K

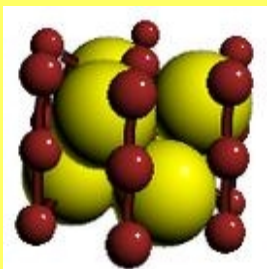


Hexagonal NiAs-type structure
(P63/mmc, #194)
 $a = 3.730 \text{ \AA}$, $c = 5.668 \text{ \AA}$, $Z=2$



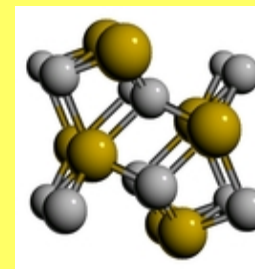
Orthorhombic MnP-structure
(Pnma, #62)
 $a = 5.72 \text{ \AA}$, $b = 3.676 \text{ \AA}$, $c = 6.379 \text{ \AA}$, $Z=4$



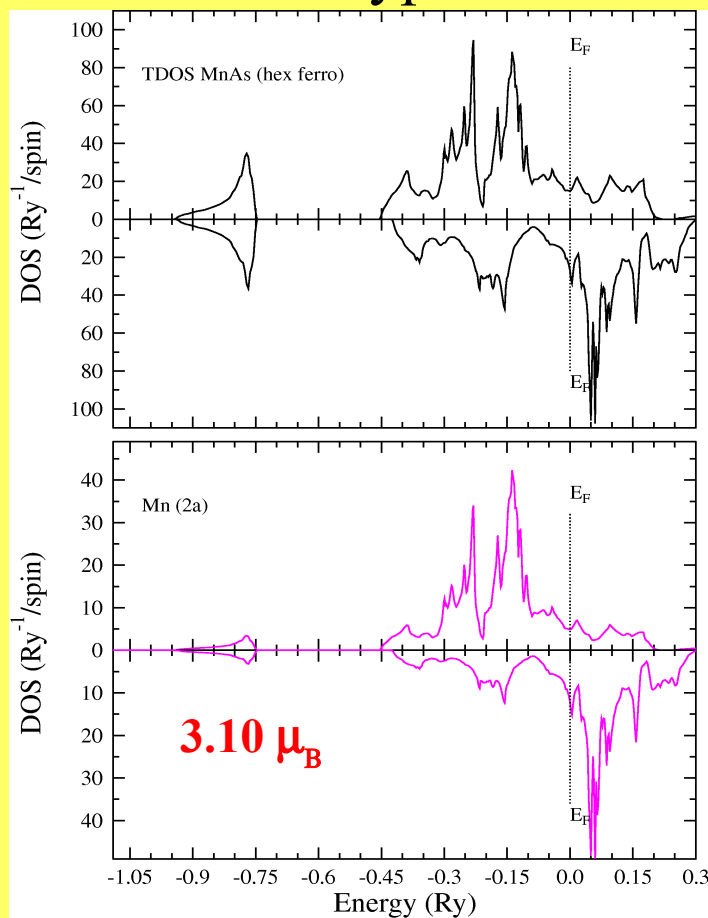


MnAs in ferro & 'paramagnetic' state

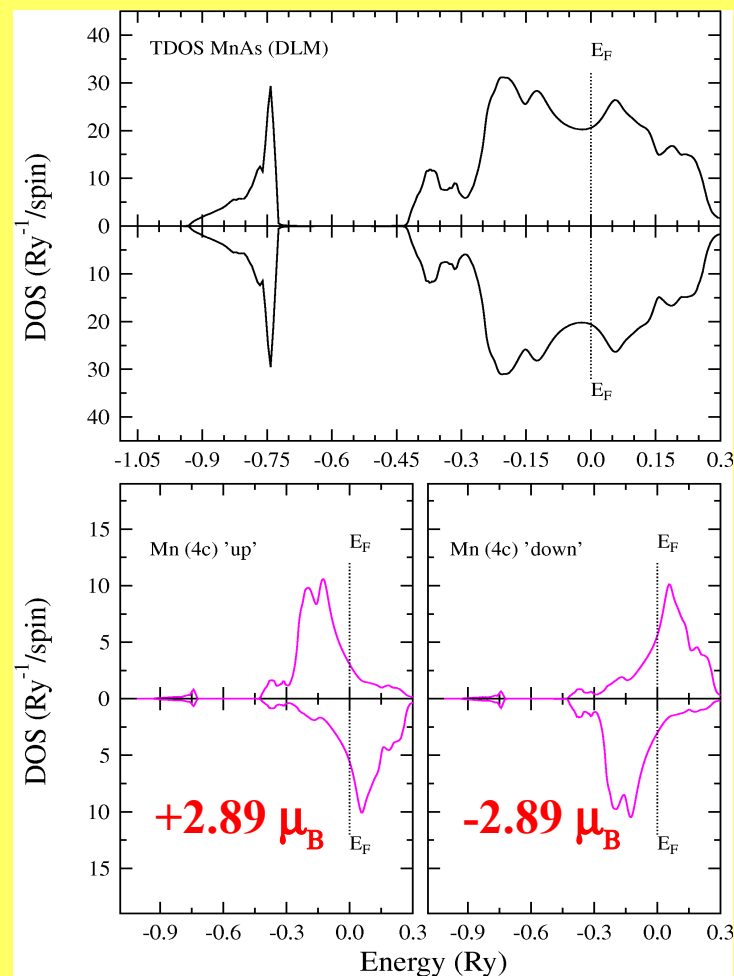
DLM (*disordered local moments*)



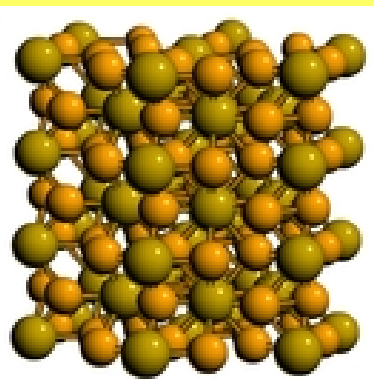
NiAs-type



MnP-type



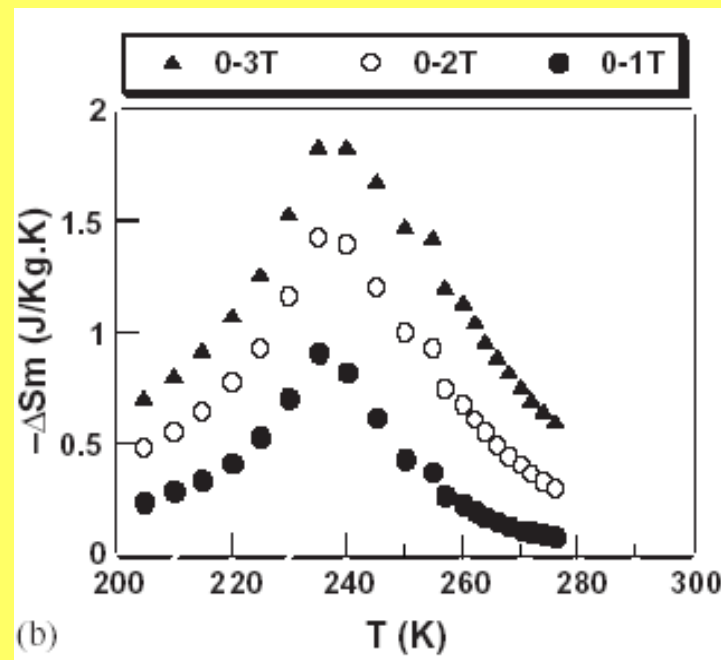
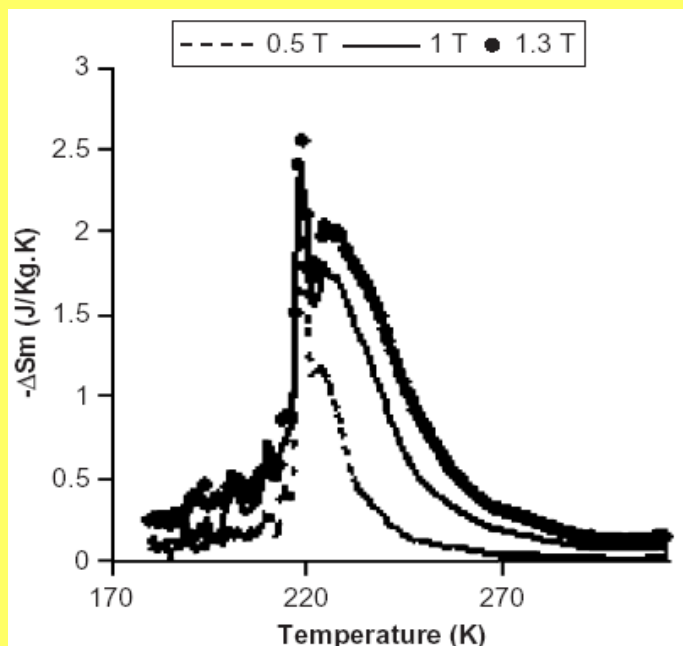
In excellent agreement with experimental data



Fe₂P (magneto-elastic transition) at 217 K

Hexagonal (P-62m, #189) $a = 5.872 \text{ \AA}$, $c = 3.460 \text{ \AA}$, $Z=3$

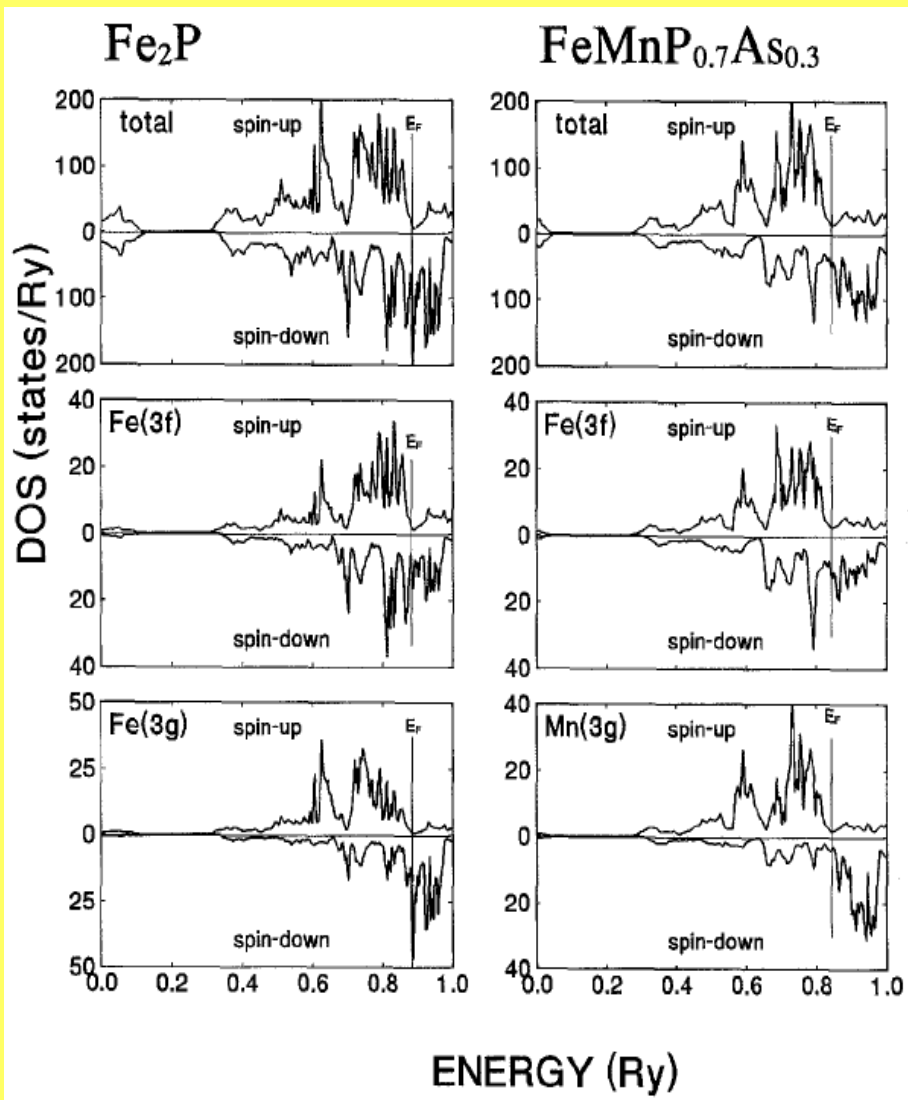
T_C increases from 217 K for Fe₂P to 235 K for Fe_{1.85}Ru_{0.15}P



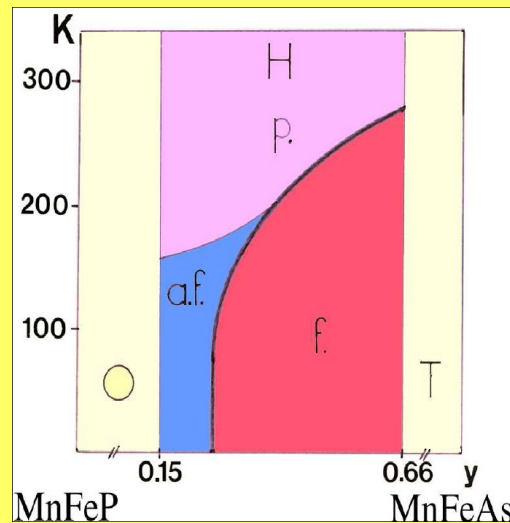
Fruchart et al., Physica A (2005)

Influence of electrons polarisation at E_F in increase of T_C , presence of small moment $0.4 \mu_B/\text{Ru}$, similar effect in Fe_{2-x}Ni_xP

Fe₂P and MnFe(P-As)



Tobola et al., JMMM (1996)



Bacmann et al., JMMM (1994)

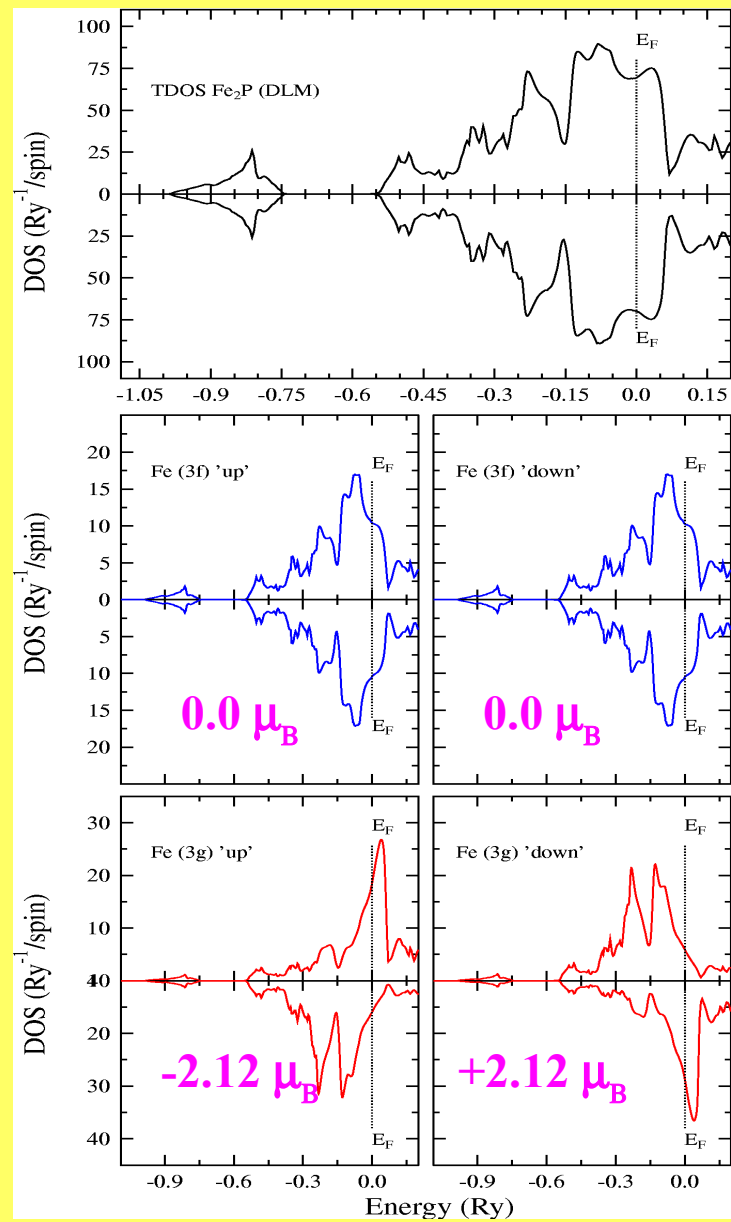
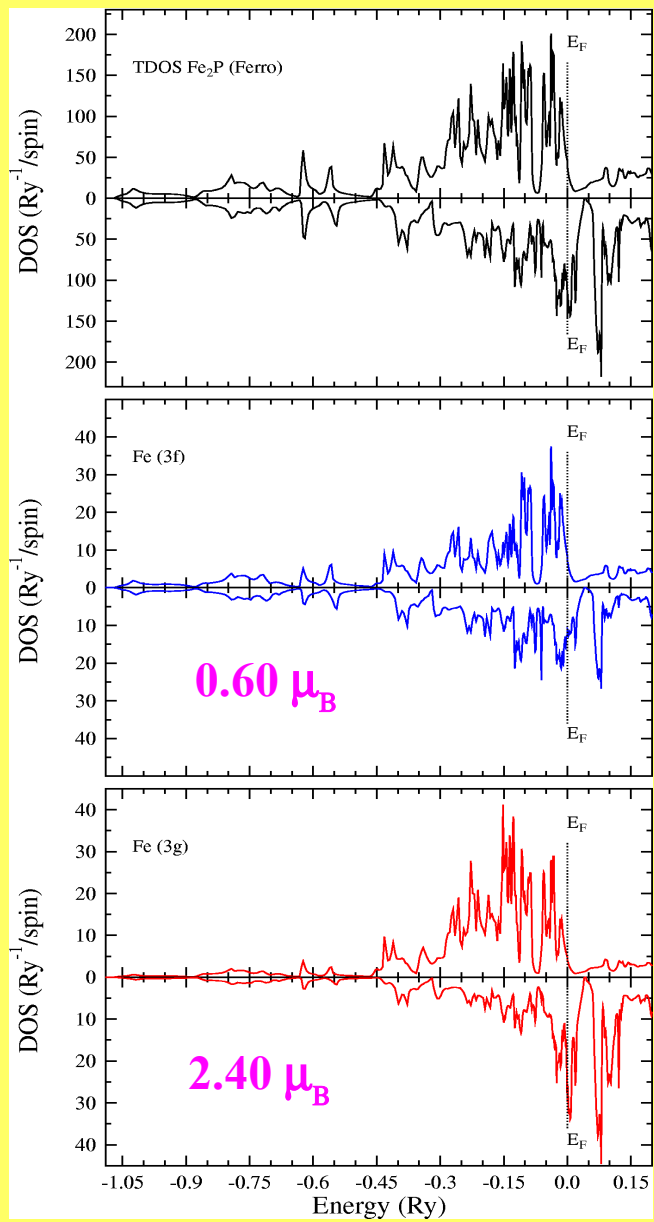
MnFe(P-As)

	Neutrons	KKR-CPA
Fe(3f)	1.24	1.25
Mn(3g)	2.55	2.95

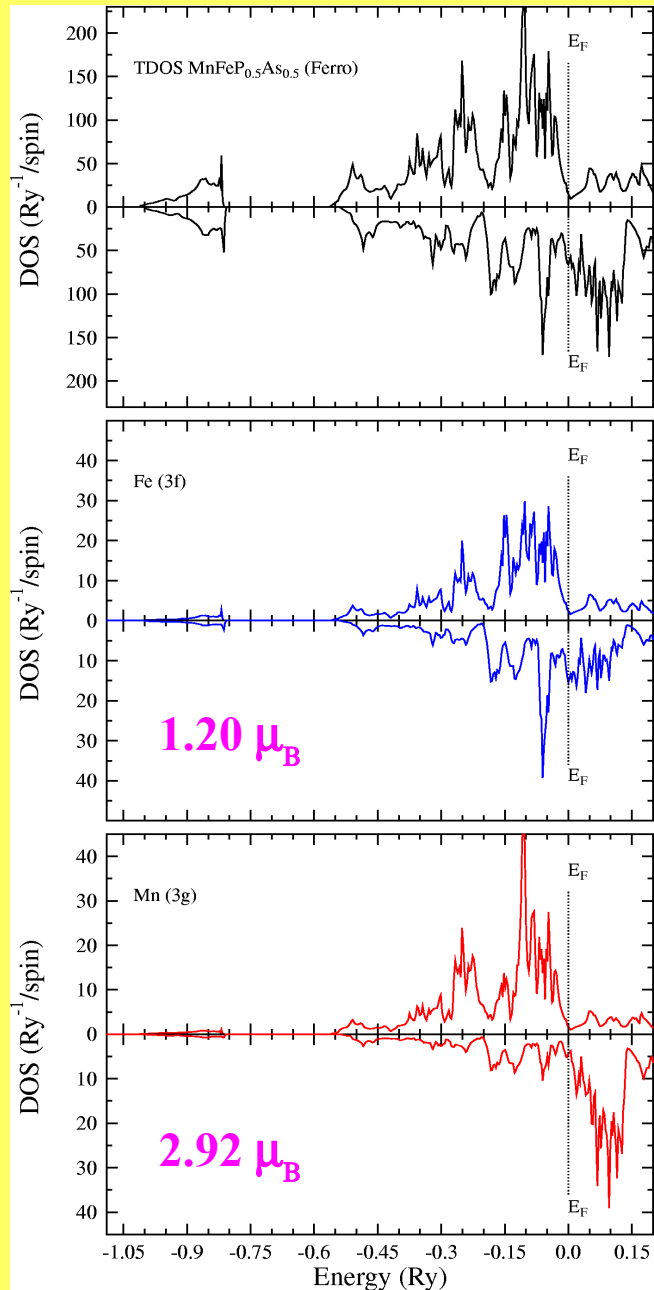
Fe₂P

	Neutrons	KKR-MT	KKR-FP
Fe(3f)	0.59	0.80	0.60
Fe(3g)	2.23	2.33	2.40

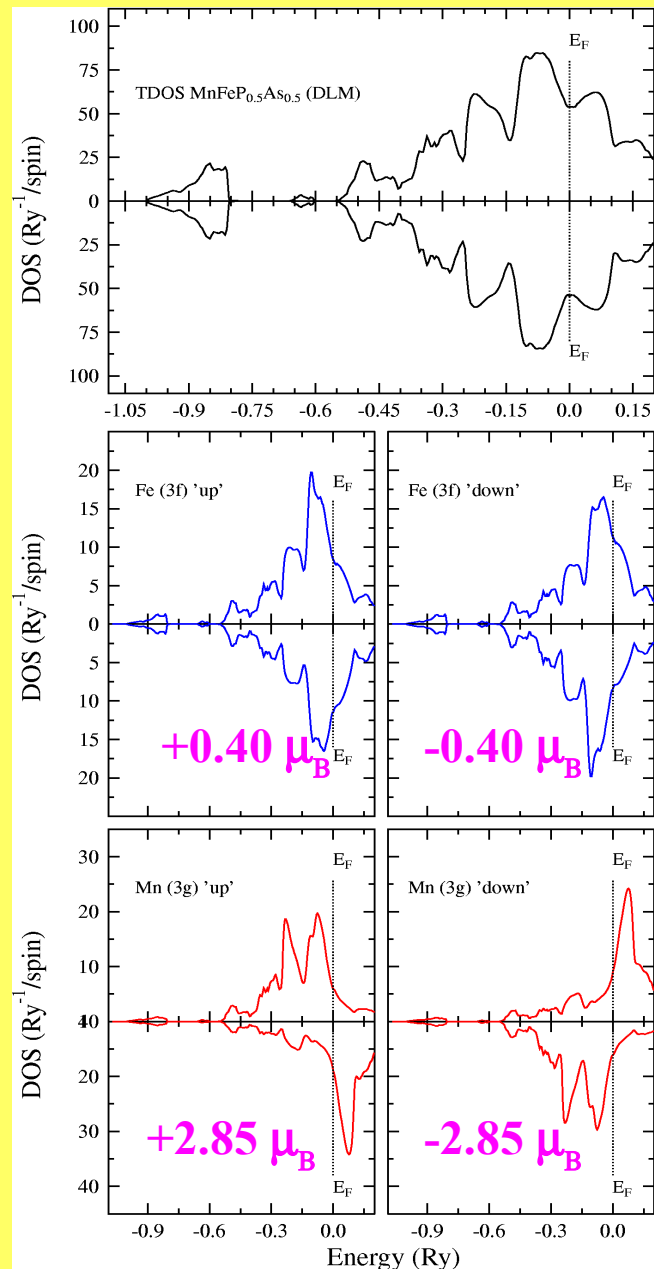
Fe₂P (ferromagnetic vs. 'paramagnetic' DLM state)



MnFe(P-As)



FM



DLM

Entropy contributions

MnAs

$$\Delta S_{\text{mag}} = R \ln(M_{\text{Mn}} + 1) = 11.3 \text{ J/(mol K)} \quad \text{since } M_{\text{Mn}} = 2.9 \mu_{\text{B}} \text{ in PM state}$$

very close to $\Delta S_{\text{exp}} = 12.8 \text{ J/(mol K)}$ from thermodynamic data

Gronvold et al., Acta Chem.Scand. (1970)

$$S_{\text{lat}} \sim 69 \text{ J/(mol K)} \quad \text{since } \Theta_{\text{D}} = 310 \text{ K} \quad \text{in NiAs-type}$$

Debye temp = ? (250 K) in MnP-type

$$\Delta S_{\text{el}} = +0.67 \text{ J/(mol K)} \quad \Delta S_{\text{el}} = +1.35 \text{ J/(mol K)} \quad \text{from } \gamma T$$

Fe₂P

$$\Delta S_{\text{mag}} = R \ln(M_{\text{Mn}} + 1) = 9.4 \text{ J/(mol K)} \quad \text{since } M_{\text{Fe(3g)}} = 2.1 \mu_{\text{B}} \text{ in PM state}$$

$$S_{\text{lat}} \sim 57 \text{ J/(mol K)} \quad \text{since } \Theta_{\text{D}} = 420 \text{ K}$$

$$\Delta S_{\text{el}} = -0.2 \text{ J/(mol K)} \quad \Delta S_{\text{el}} = -0.6 \text{ J/(mol K)} \quad \text{from } \gamma T$$

$$\Delta S_{\text{mag}}(\text{exp}) = 0.36 \text{ J/(mol K)} \quad B = 1.3 \text{ T}$$

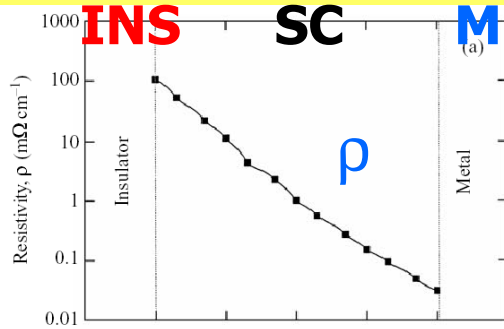
Własności termoelektryczne



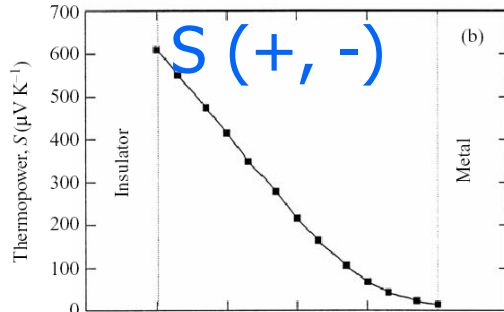
A. Joffe

$$ZT = \frac{S^2}{\rho \kappa}$$

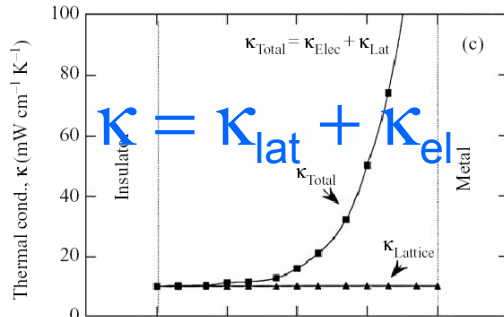
Oporność



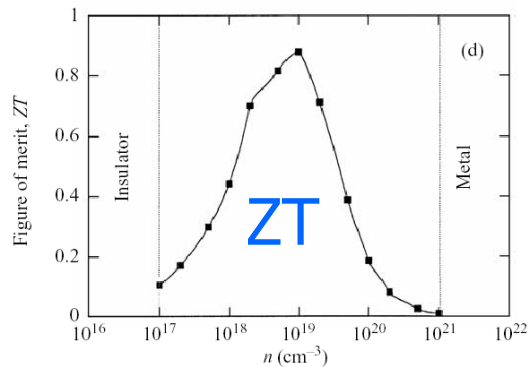
Siła TE



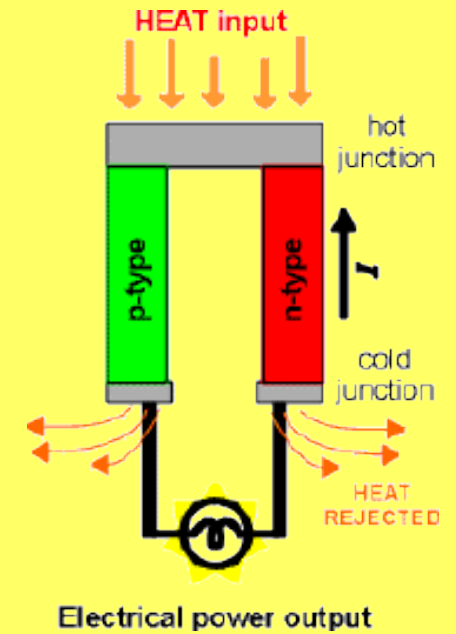
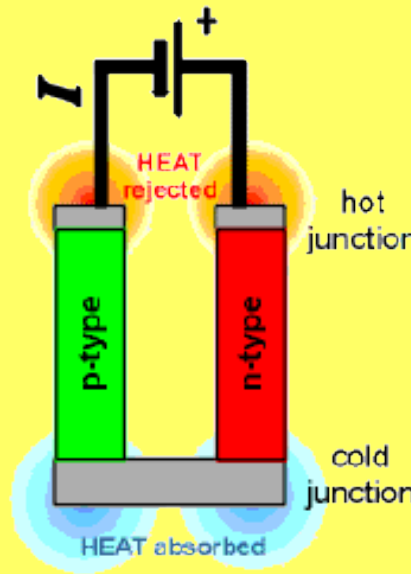
Przewod. cieplna



ZT „dobroć”



Electrical power input



ELEMENTY CHŁODZĄCE

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

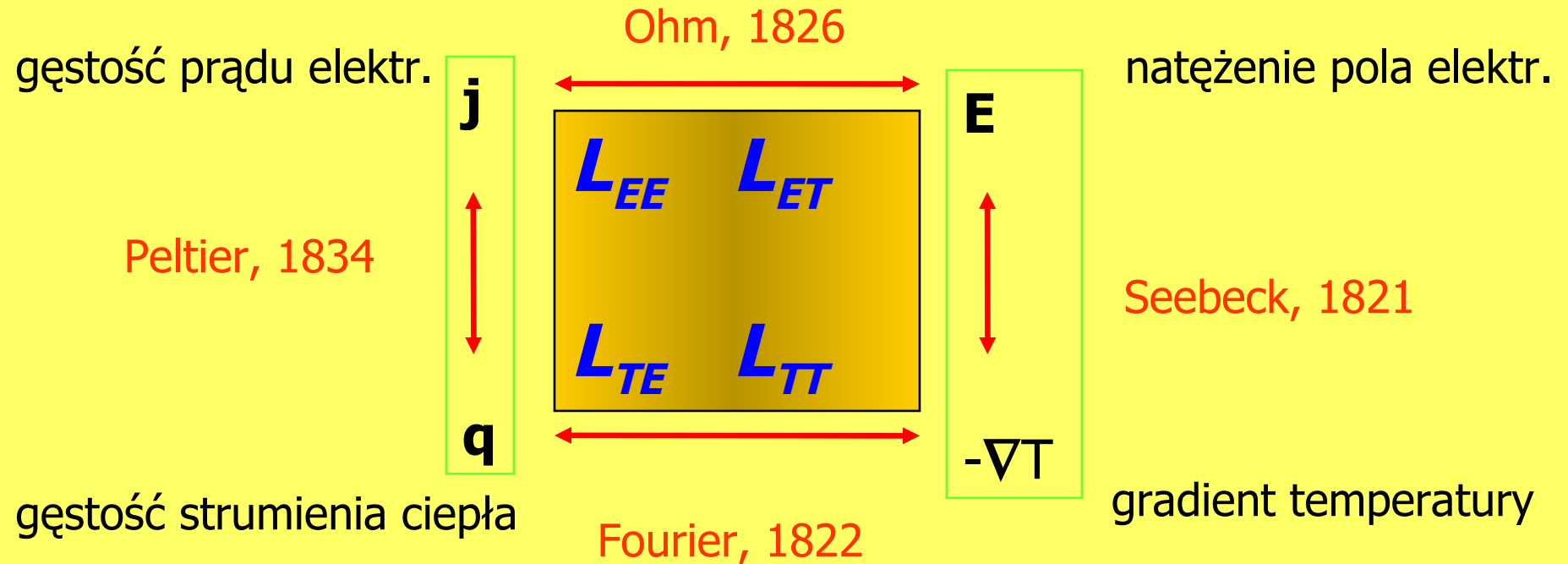
$$\gamma = (1 + ZT)^{1/2}$$

ŹRÓDŁA ENERGII ELEKTR.

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

„Czworobok” termoelektryczny

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} E \rightarrow \\ -\nabla T \end{bmatrix}$$



$$\mathbf{S} = \Pi / T \quad (\text{Kelvin-Onsager})$$

$$L_{ET} = L_{TE} / T$$

$$\kappa / \sigma \approx L_0 T \quad (\text{Wiedemann-Franz, } L_0 \text{ liczba Lorentza}) \quad \kappa \approx -L_{TT}$$

Volta (1800) - ogniwo, Ampere (1820) – dwa przewodniki z prądem,
Faraday (1831), Gauss (1832), ...

$$\begin{bmatrix} \dot{I} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} E \rightarrow \\ -\nabla T \end{bmatrix}$$

Efekt Seebecka (1821)



1770 Tallin
1854 Berlin

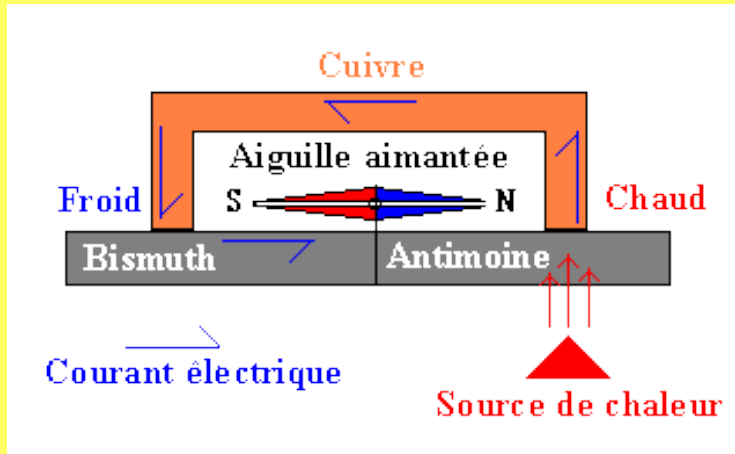
natężenie pola elektr.

$$\mathbf{E} = S \nabla T$$

gradient temperatury

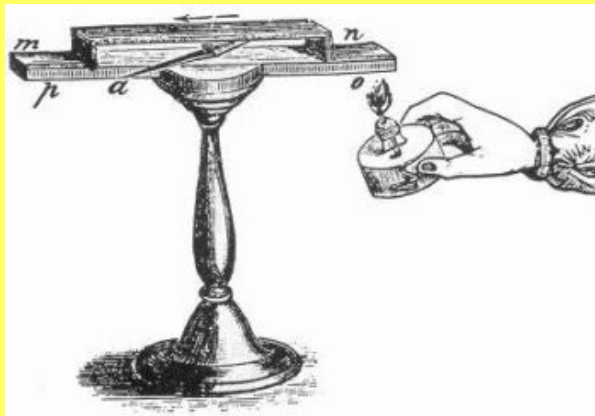
siła termoelektryczna

$$S = L_{EE}^{-1} L_{ET}$$



Barwna postać romantyzmu

- wraz z Goethe tworzy nową teorię barw (przeciwną Newtonowi),
- gradient temperatur powoduje zmiany pola magnetycznego Ziemi !!,
- doświadczenia Oersteda (1820) – „oślepiają” uczonych;



Wyjaśnienie : termomagnetyzm - „magnetyczna” polaryzacja metali i stopów wskutek różnicy temperatur !!

$$\begin{bmatrix} \dot{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} E \rightarrow \\ -\nabla T \end{bmatrix}$$

Efekt Peltier (1834)

zegarmistrz

strumień ciepła

$$\mathbf{q} = \Pi \mathbf{j}$$

gęstość prądu

współczynnik Peltier

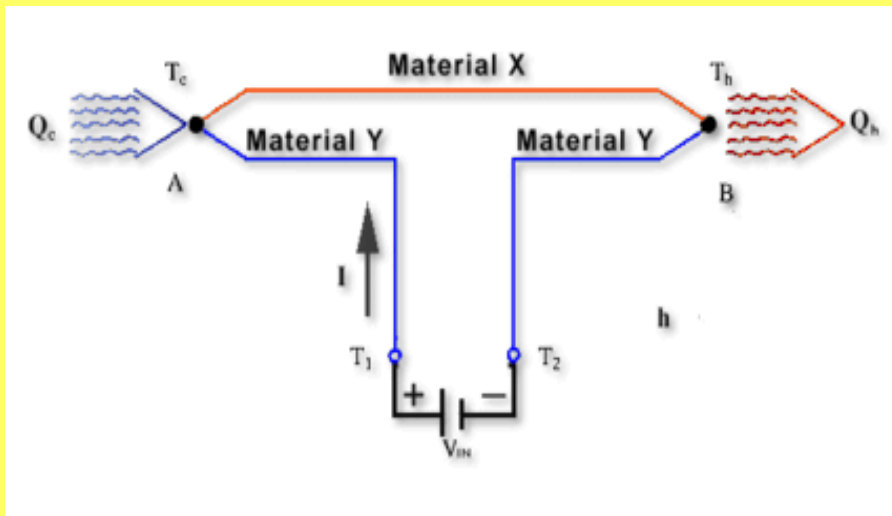
$$\Pi = L_{TE} L_{EE}^{-1}$$

1785 Ham
1845 Paris

odwrotny proces do efektu Seebecka

Efekt Thomsona (1834)

wydzielanie się ciepła w obecności prądu \mathbf{j} i gradientu temperatury dT/dx



$$Q = j^2/\sigma + \mu j dT/dx$$

Joule Thomson

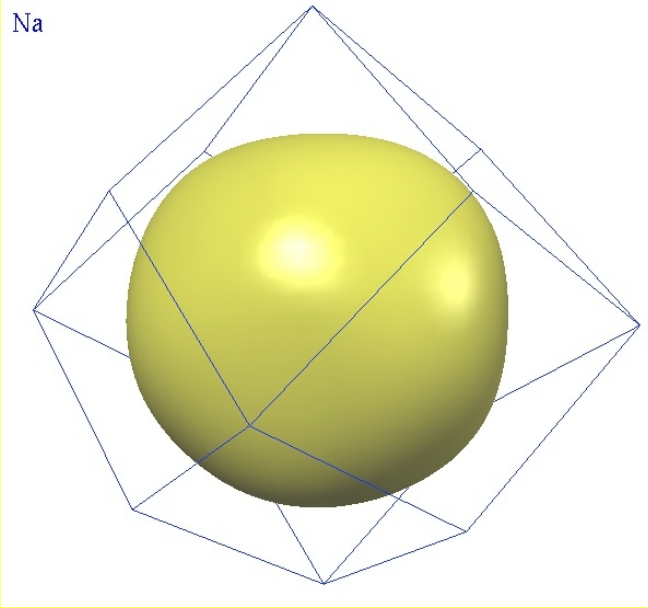
$$\mu = T dS/dT$$

$$\Pi = T S$$

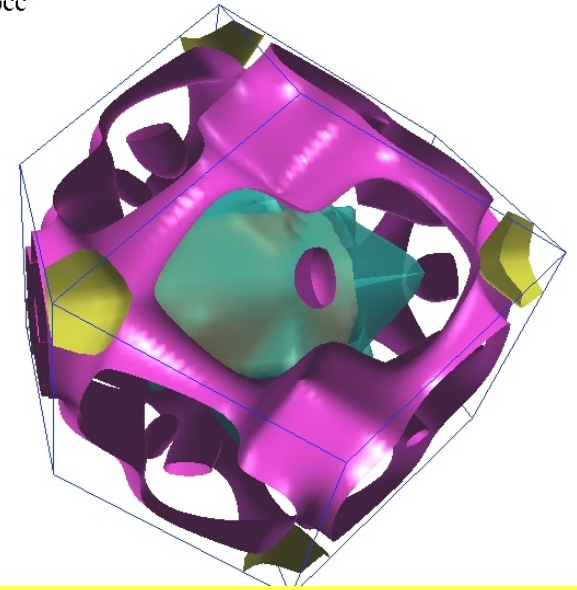
$$L_{ET} = L_{TE}/T$$

Badanie stanów elektronowych w pobliżu powierzchni Fermiego $E(\mathbf{k})=E_F$

Na



Fe_bcc



$$E(\mathbf{k}) = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}$$

Ruch elektronów w ciele stałym

Prędkość elektronów

$$\mathbf{v}_g = \frac{d\omega}{d\mathbf{k}} = \frac{1}{\hbar} \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}} = \nabla_{\mathbf{k}} E(\mathbf{k}) = \mathbf{v}(\mathbf{k})$$

$$\mathbf{v} = \frac{\hbar \mathbf{k}}{m^*} \Leftrightarrow E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m^*} \quad \mathbf{v}(\mathbf{k}) \text{ równoległe } \mathbf{k} \text{ (sferyczna powierzchnia Fermiego)}$$

W ogólności \mathbf{v} **nie jest** równoległe do \mathbf{k} (np. elipsoida), jest prostopadła do powierzchni izoenergetycznej $E(\mathbf{k})$

Przyspieszenie elektronów

$$\mathbf{F} = \hbar \frac{d\mathbf{k}}{dt} \Rightarrow \mathbf{a}_k = \frac{d\mathbf{v}_k}{dt} = \frac{1}{\hbar} \frac{\partial^2 E(\mathbf{k})}{\partial \mathbf{k} \partial \mathbf{k}} \frac{d\mathbf{k}}{dt} = \frac{1}{\hbar^2} \frac{\partial^2 E(\mathbf{k})}{\partial \mathbf{k} \partial \mathbf{k}} \mathbf{F}$$

$$\mathbf{a}_k = (\mathbf{m})^{-1} \mathbf{F} \quad \text{gdzie} \quad (m_{ij})^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}$$

W ogólności tensor masy efektywnej jest **niezależny** od prędkości elektronu

$$n(E_F) \propto \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}}$$

$$(m_{ij})^{-1} \propto \frac{\partial^2 E}{\partial k_i \partial k_j}$$

Gęstość stanów dla $E=E_F$ można uzyskać w pomiarach **ciepła właściwego oraz podatności paramagnetycznej**

Masy efektywne można uzyskać w pomiarach **dHvA oraz pomiarach transportowych**

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ \nabla T \end{bmatrix}$$

Kinetyczna teoria Zimana

$$\sigma(T) = e^2/3 \int dE N(E) v^2(E) \tau(E, T) [-\partial f(E)/\partial E]$$

Przewodność elektryczna

$$S(T) = e(3T\sigma)^{-1} \int dE N(E) v^2(E) E \tau(E, T) [-\partial f(E) / \partial E] =$$

$$(3eT\sigma)^{-1} \int dE \sigma(E, T) E [-\partial f(E) / \partial E]$$

Siła termoelektryczna (współczynnik Seebecka)

$$N(E) = (2\pi)^{-3} \int \delta(E(\mathbf{k}) - E) d\mathbf{k}$$

DOS (density of states)

Przewodność cieplna

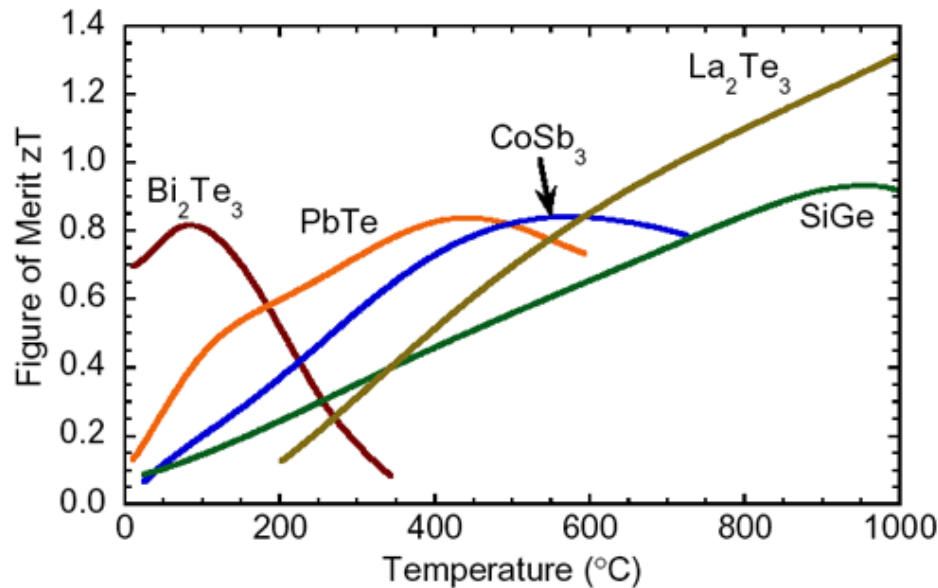
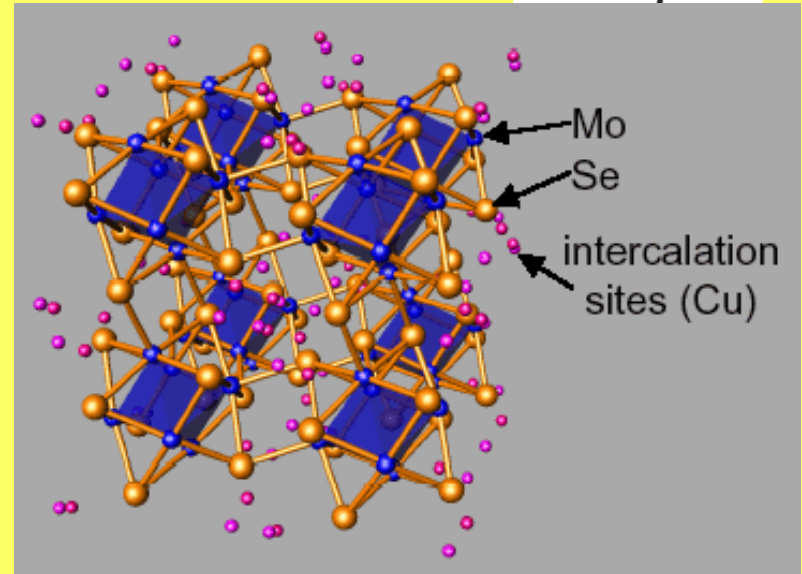
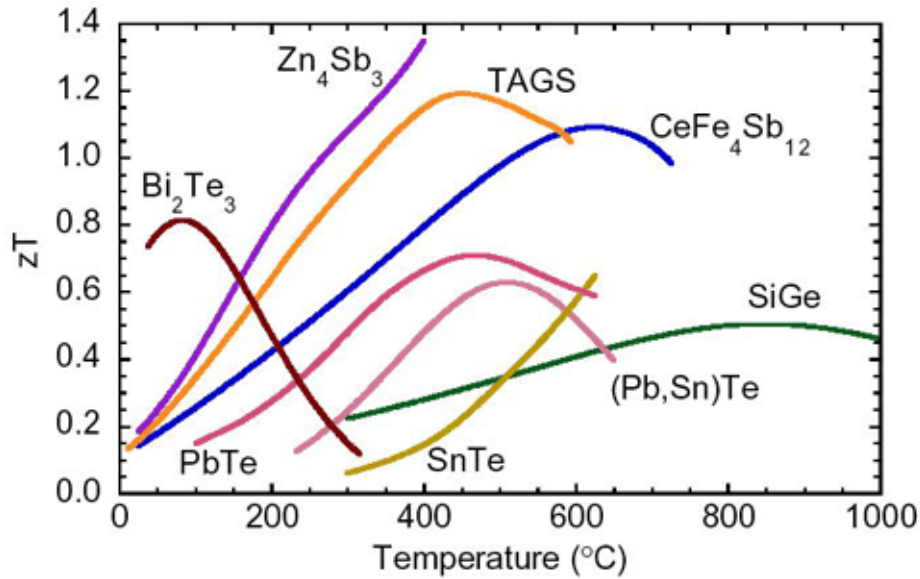
$$\kappa/\sigma \approx L_0 T, \quad L_0 = 2.45 \quad \kappa \approx -L_{TT}$$

prawo Wiedemanna-Franza, L_0 liczba Lorentza

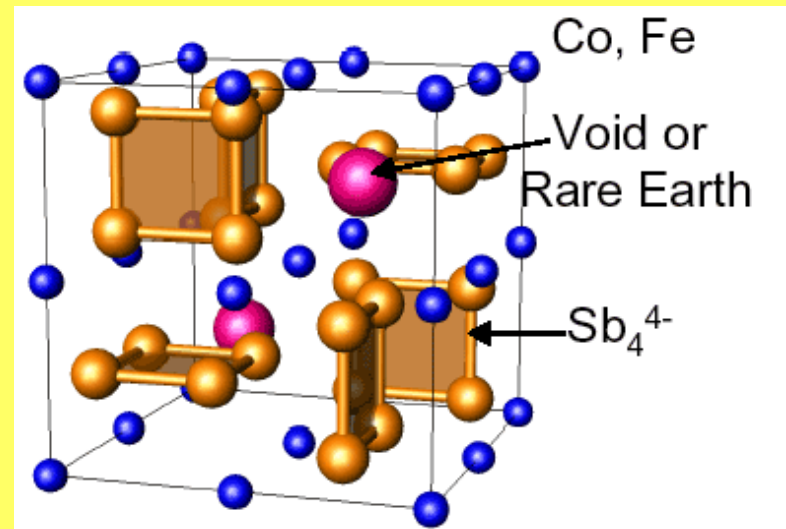
Przybliżenie czasu relaksacji w równaniu Boltzmanna

Materialy TE

$$ZT = \frac{S^2}{\rho \kappa}$$



Chevrel phases



Skutterudites

J. Snyder, JPL-NASA

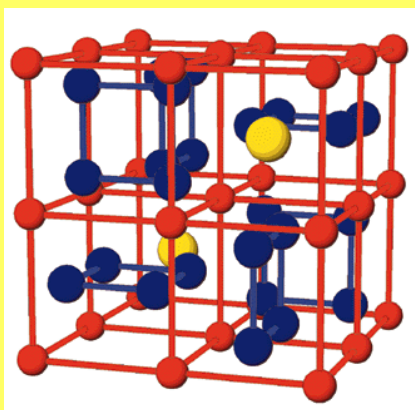
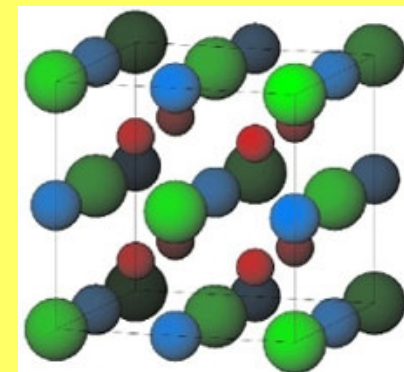
Electronic structure peculiarities

Half-Heusler (VEC=18)

Semiconductors/semimetals

(CoTiSb, NiTiSn, FeVSb, ...)

$$\underline{9 + 4 + 5 = 18}$$



Skutterudites (VEC=96)

semiconductors/semimetals

(CoSb₃, RhSb₃, IrSb₃, CoP₃ ...)

$$\underline{4 \times 9 + 12 \times 5 = 96}$$

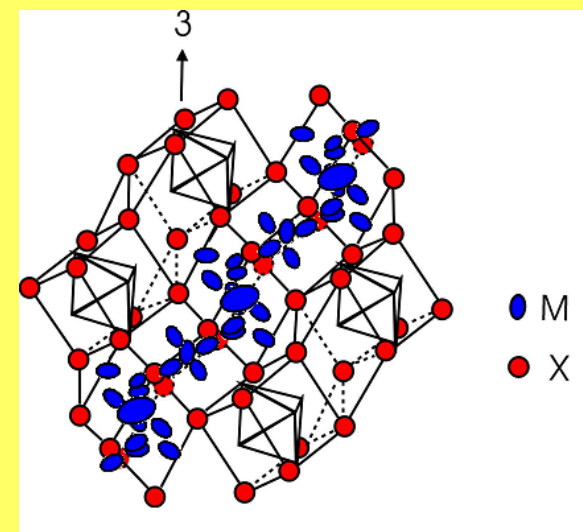
Chevrel phases (VEC=72)

semiconductors/semimetals

(TiMo₆Se₈, Zn₂Mo₆Se₈, ...)

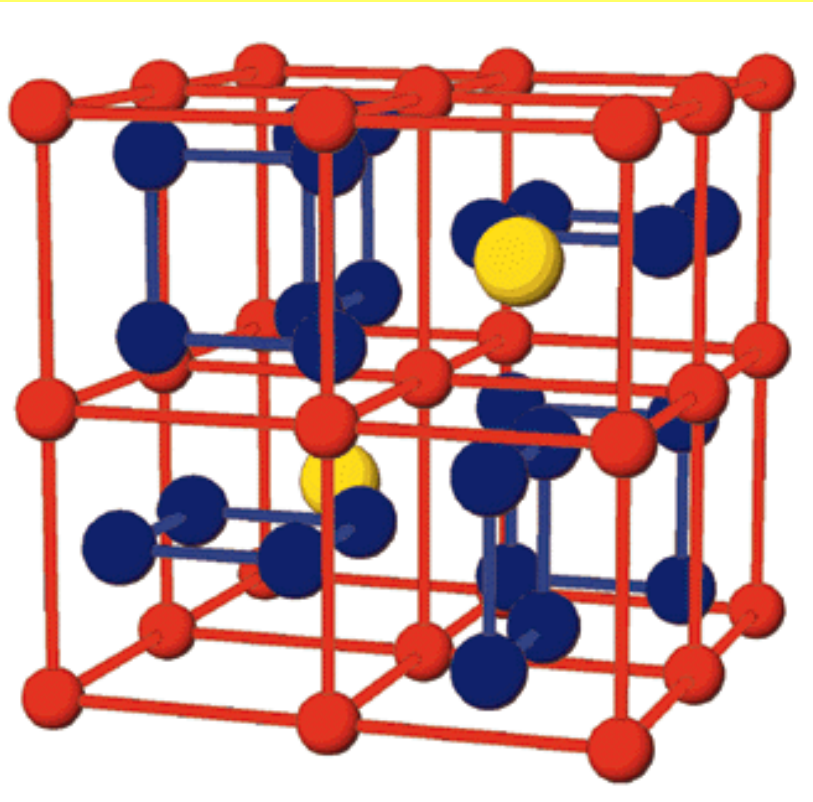
$$\underline{8 \times 4 + 6 \times 6 = 68} \text{ (} p\text{-}d \text{ Mo}_6\text{Se}_8\text{)}$$

4 holes to energy gap



Skutterudyty: prototyp - minerał CoAs_3

Nazwa od miejscowości **Skutterud** (Norwegia), ważny kruszec kobaltu



Najbardziej badane układy termoelektryczne w ostatnich 15 latach (**USA, Japonia**, Niemcy, Francja, ..., Polska),
- najbliższe realizacji koncepcji Slacka (1995): **PGEC = „phonon-glass electron crystal”**
- **przewodnictwo elektryczne** jak w metalach (domieszkowanie) – znakomite,
- **siła termoelektryczna** – duża (poziom Fermiego w pobliżu przerwy energet.)
- **przewodnictwo cieplne** jak w amorfikach – słabe, specyficzna dynamika sieci – rozpraszanie fononów poprzez „**rattling**”

Im-3 space group

No. 204 (bcc)

Co : 8c (1/4,1/4,1/4)

Sb : 24g (0,u,v)

void: 2a (0,0,0)

$u=0.335, v=0.159$

Filled skutterudites

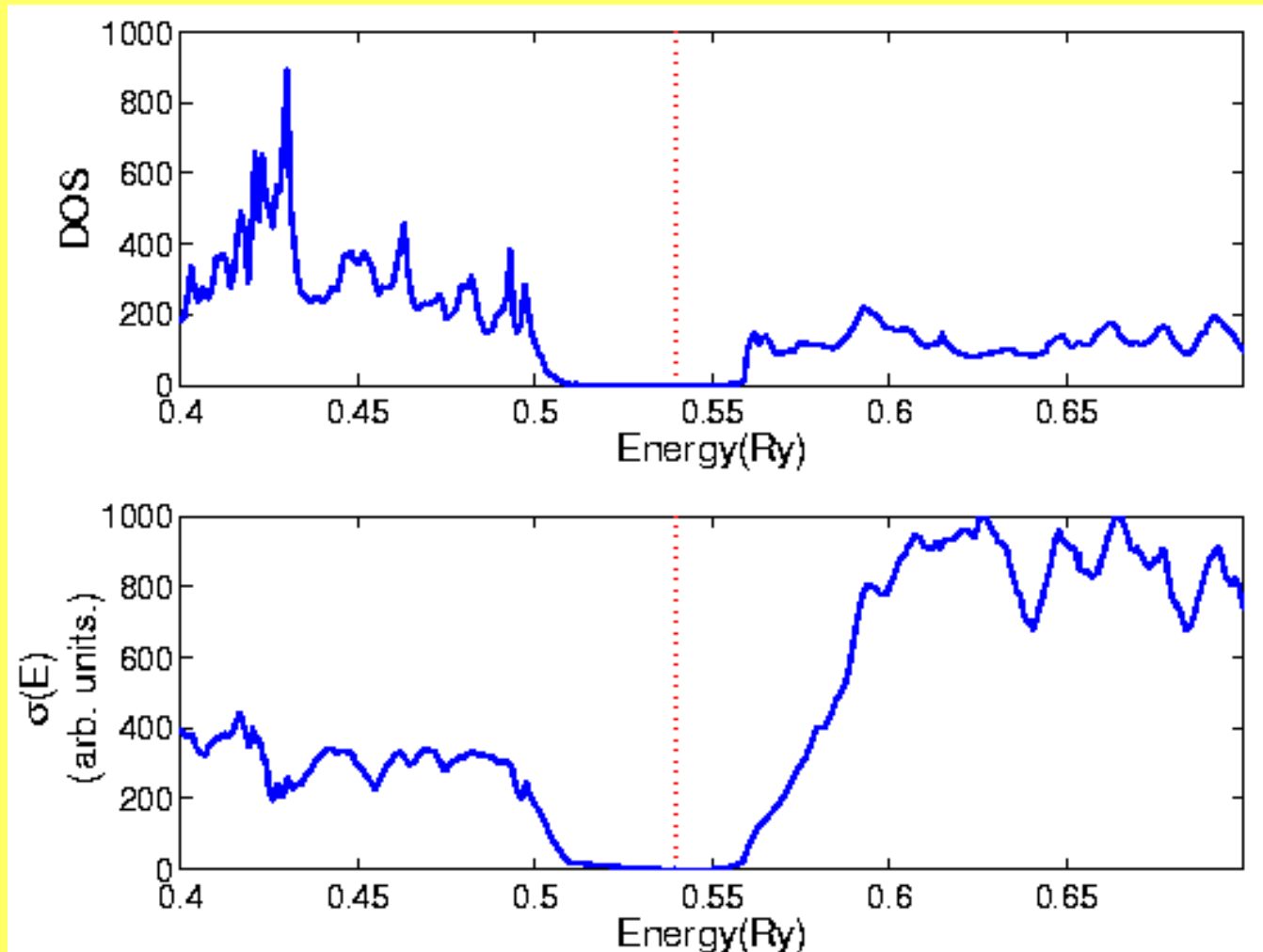
RT_4X_{12} (e.g. $\text{LaFe}_4\text{Sb}_{12}$)

Fe : 8c (1/4,1/4,1/4)

Sb : 24g (0,u,v)

La: 2a (0,0,0)

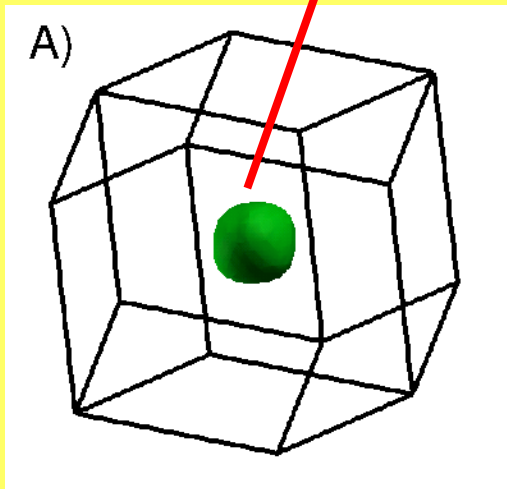
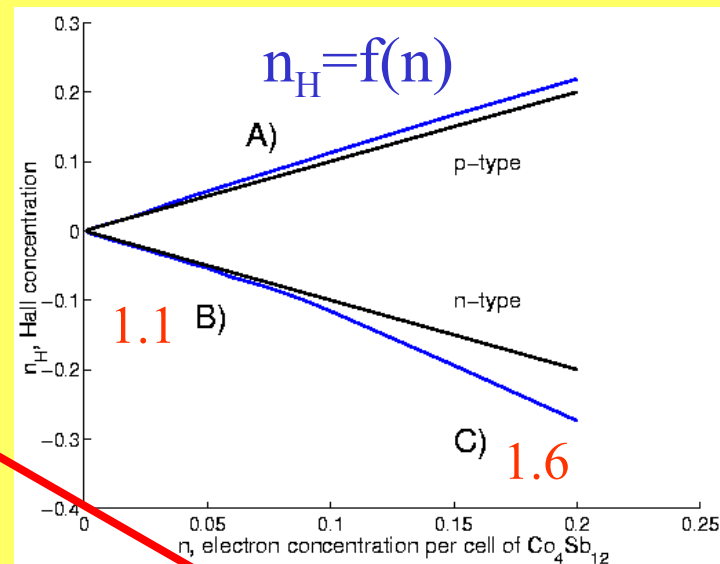
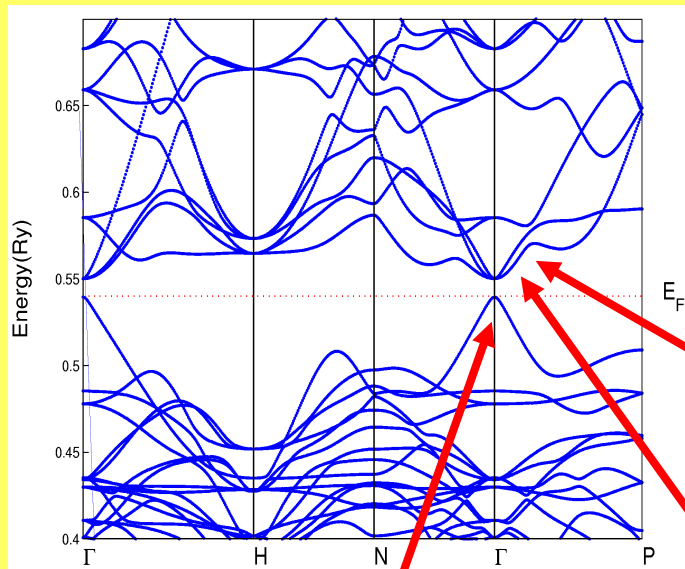
Density of states **DOS** vs. transport function $\sigma(E)$



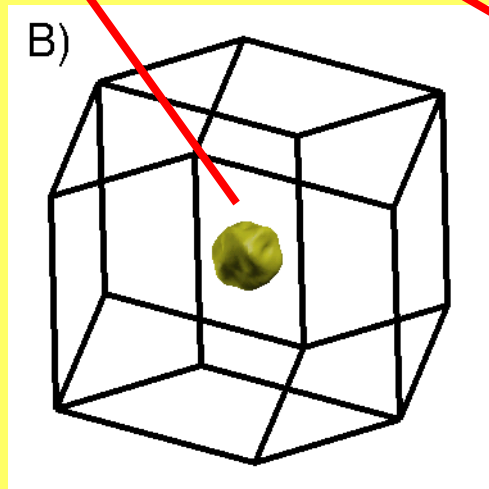
Small substitution **0.01-0.05** el./Co₄Sb₁₂ $\rightarrow \Delta E_F \approx$ **1-2** mRy

Doped CoSb_3 : FS vs. Hall concentration

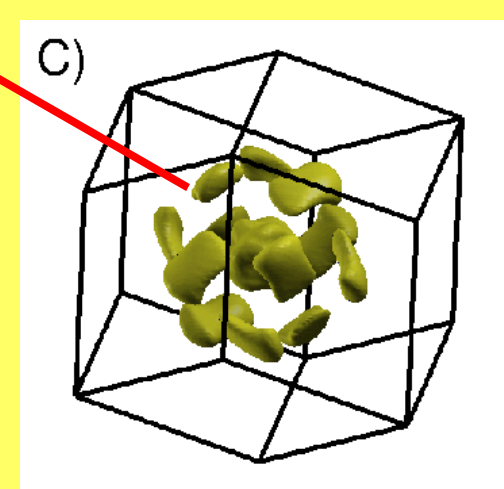
L.Chaput, ... J.T., PRB (2005)



$E_F = 0.5191$ Ry, $n = 0.01$



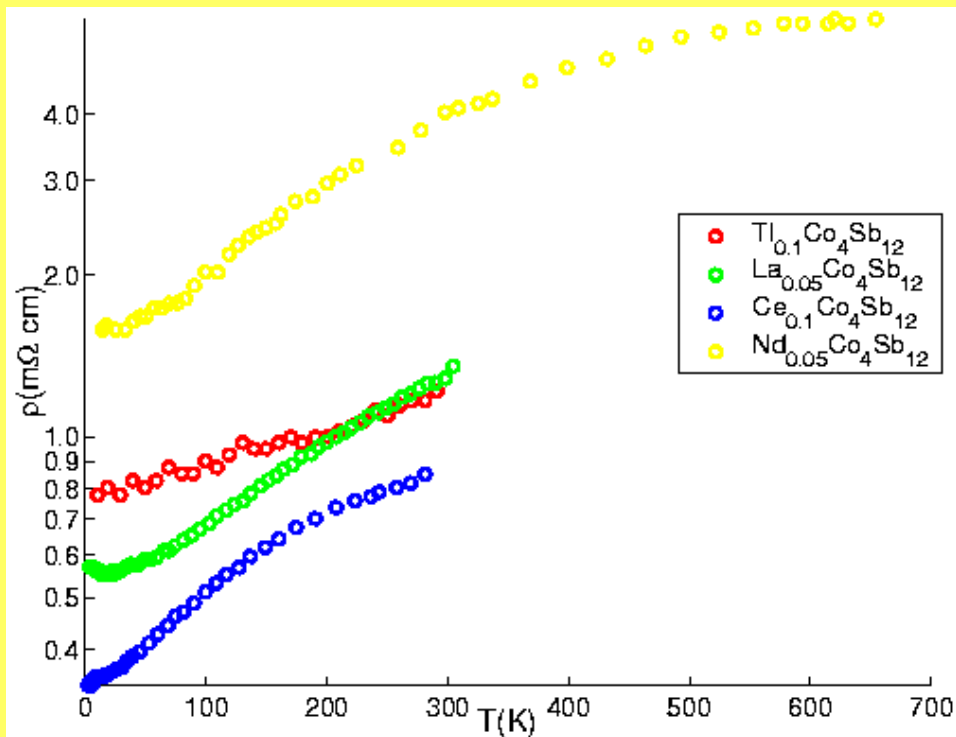
$E_F = 0.5570$ Ry, $n = 0.01$



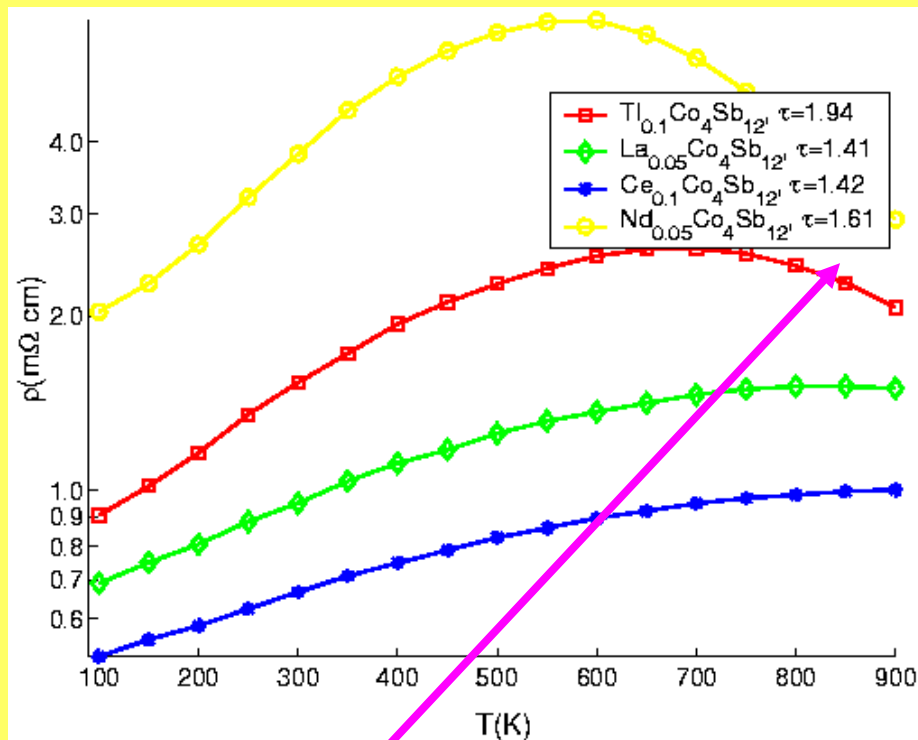
$E_F = 0.5585$ Ry, $n = 0.06$

Doped CoSb_3 : electrical resistivity

Ekperyment (z literatury)



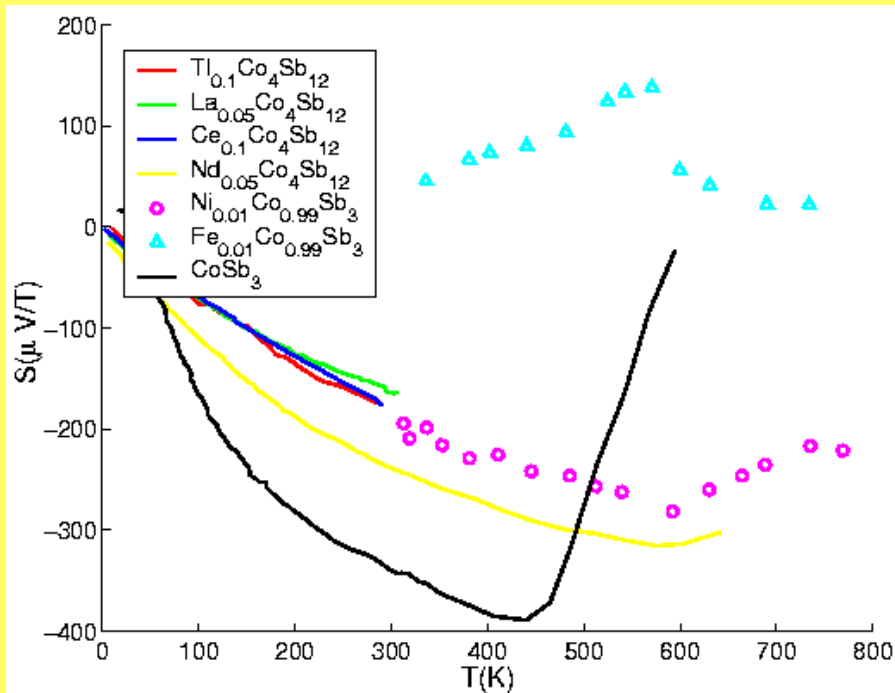
Obliczenia



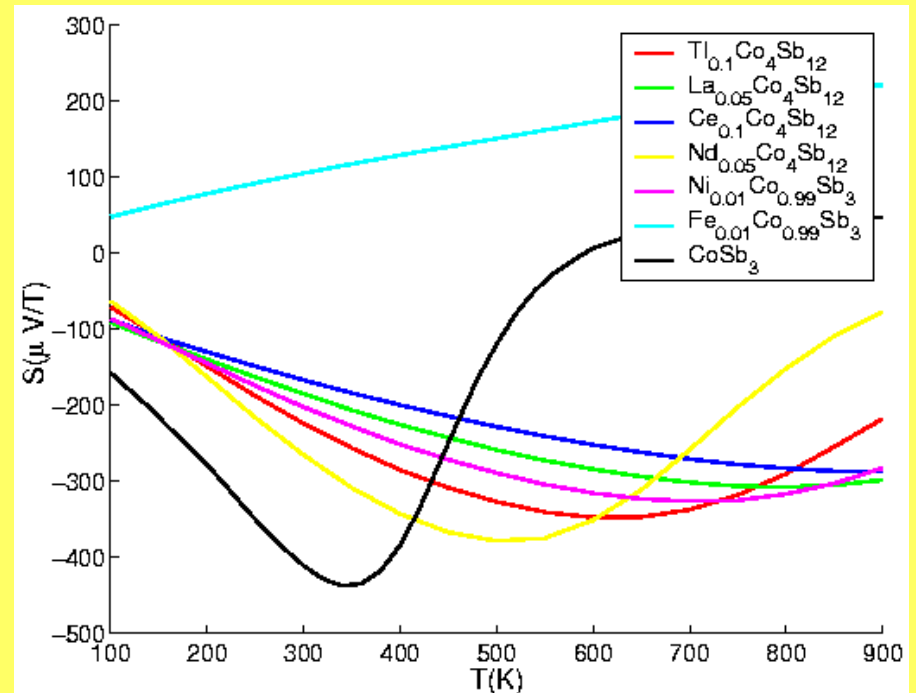
Przybliżenie stałego czasu relaksacji (jedyne swobodny parametr) dobieramy tak aby zgodność z krzywymi eksper. była satysfakcjonująca ($t = 10^{-14}$ s)

Doped CoSb₃ : thermopower

Experiment



Theory



Przybliżenie stałego czasu relaksacji nie ma znaczenia, bo współczynnik Seebecka od niego NIE ZALEŻY – znakomity test dla teorii !!!

Heusler phases X_2YZ , XYZ (1903)

DO_3 structure

$Fm\bar{3}m$ (typ Fe_3Al)

X : $(0,0,0), (1/2,1/2,1/2)$

X : $(3/4,3/4,3/4)$

Z : $(1/4,1/4,1/4)$

Normal Heusler $L2_1$

$Fm\bar{3}m$ (typ Cu_2MnAl)

X : $(0,0,0), (1/2,1/2,1/2)$

Y : $(3/4,3/4,3/4)$

Z : $(1/4,1/4,1/4)$

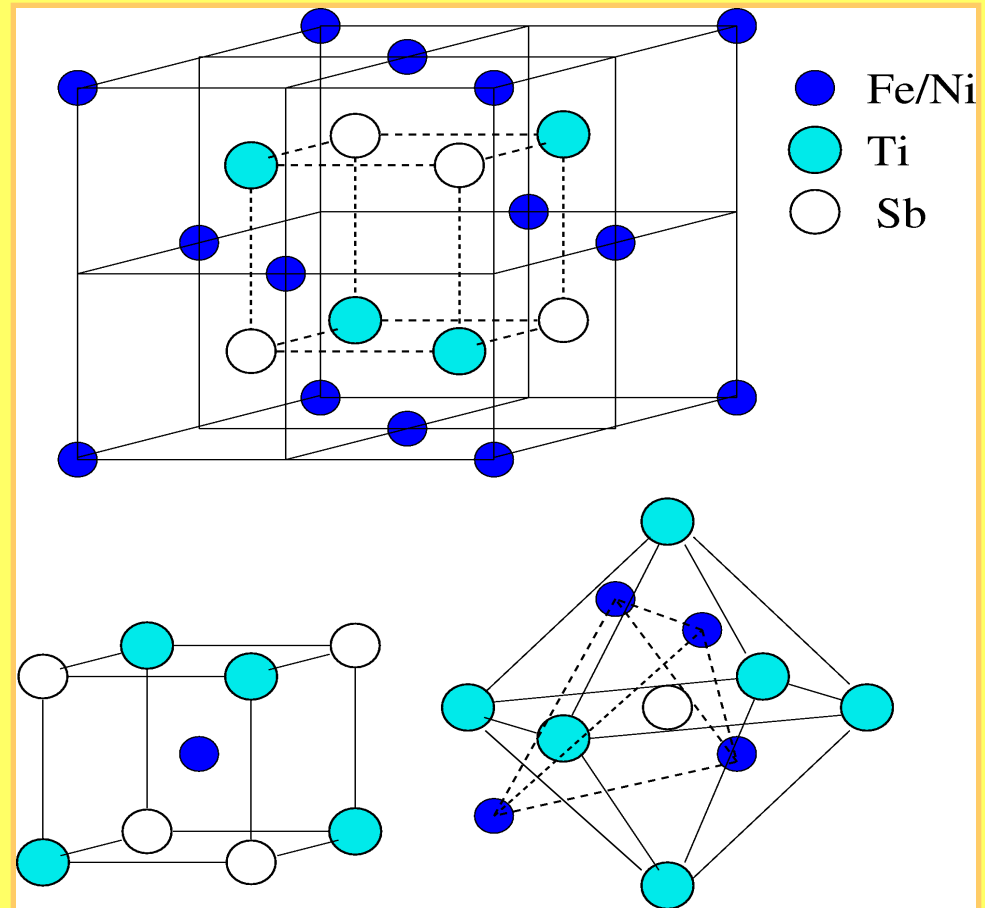
Half-Heusler $C1_b$

$F\bar{4}3m$ (typ $AgMgAs$)

X : $(0,0,0)$ 4a

Y : $(3/4,3/4,3/4)$ 4d

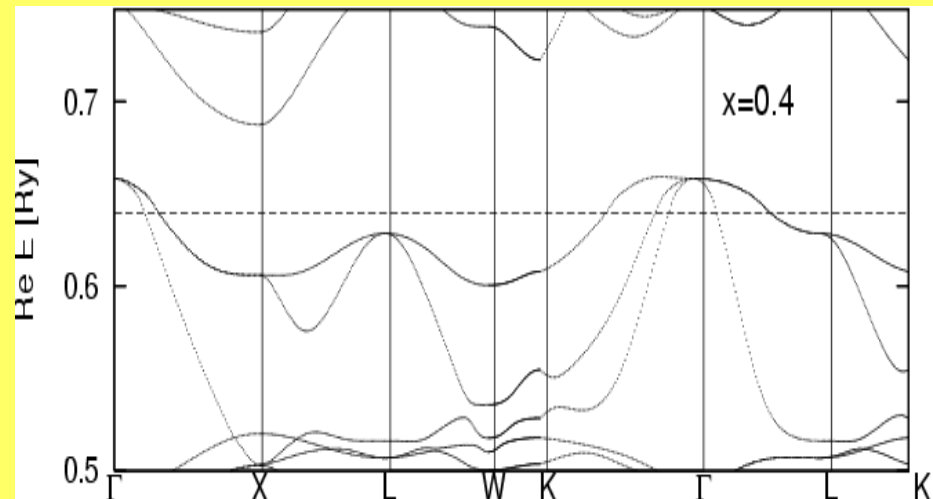
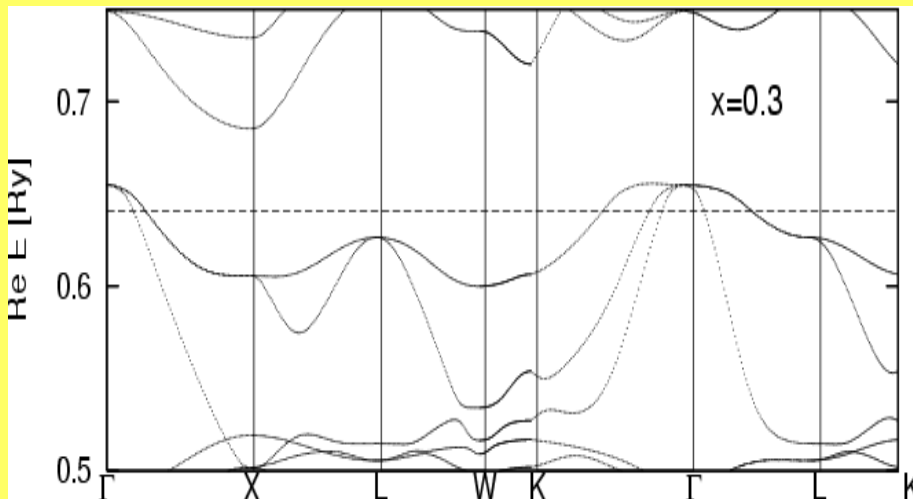
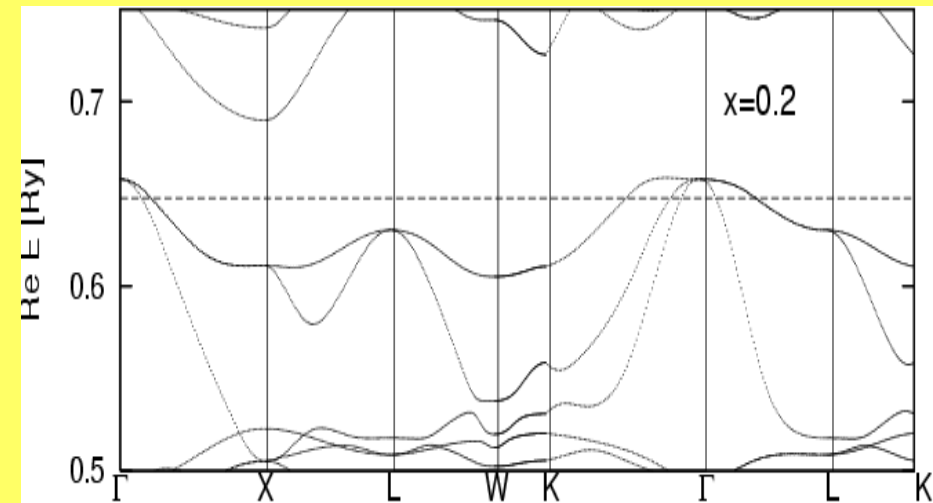
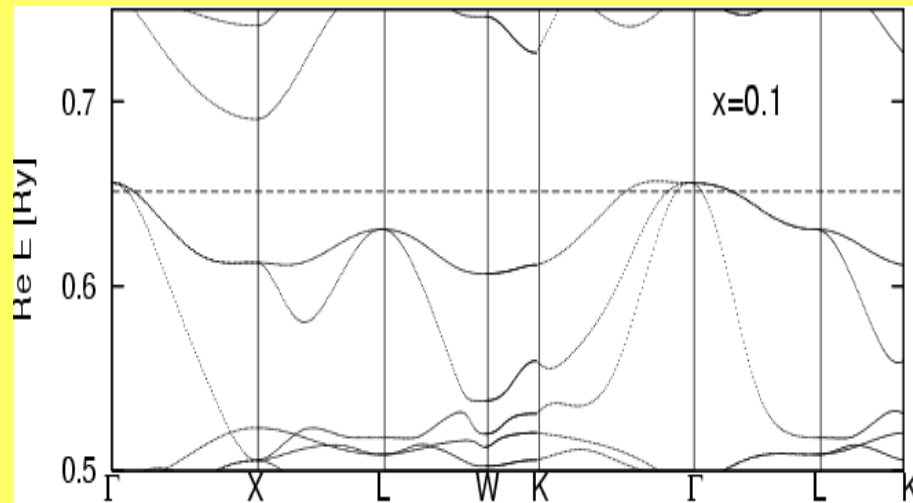
Z : $(1/4,1/4,1/4)$ 4c



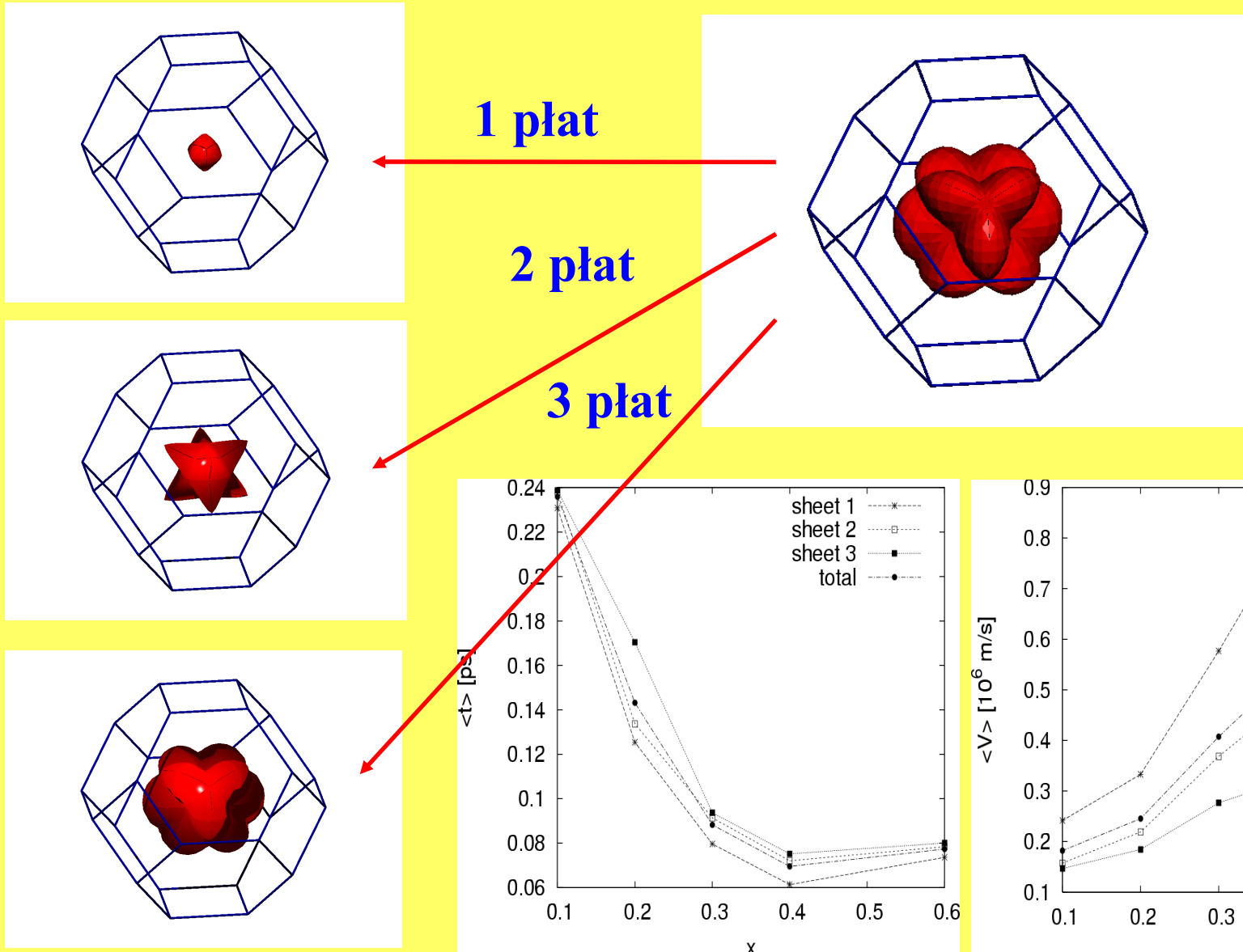
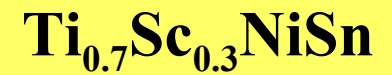
Crystal stability
 sp^3 , d orbitals

Przejście półprzewodnik-metal $\text{Ti}_{1-x}\text{Sc}_x\text{NiSn}$

W stopach nieuporządkowanych $E(k)$ są pasmami o zespolonej energii
 $\text{Re } E(k) \rightarrow$ **prędkość grupowa** ; $\text{Im } E(k) \rightarrow$ **czas życia nośników**



Prędkości i czasy życia (FS)



Semiconductor to metal transition in (Ti-Sc)NiSn half-Heusler

Thermopower

Resistivity

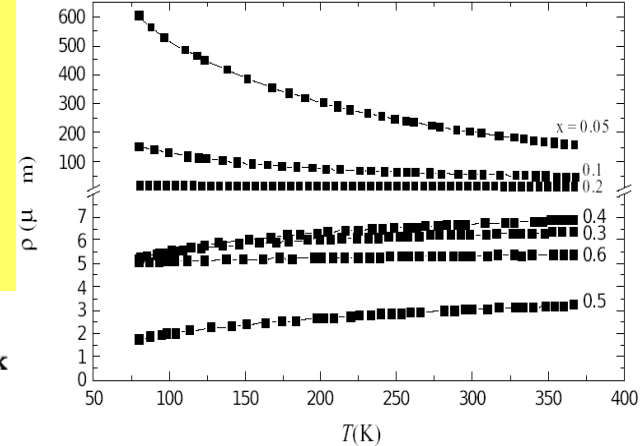
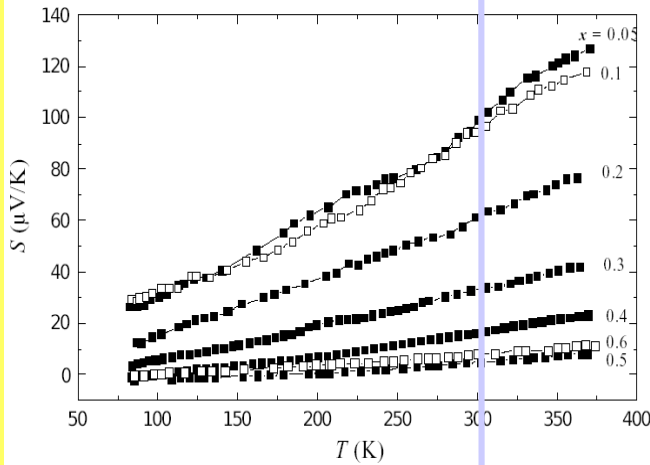
Horyn et., JALCOM (2004)

Experiment

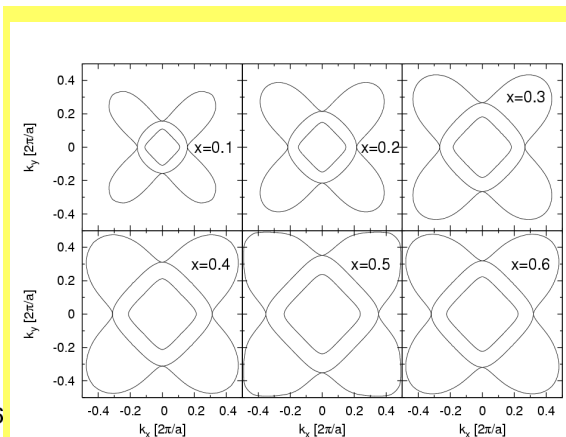
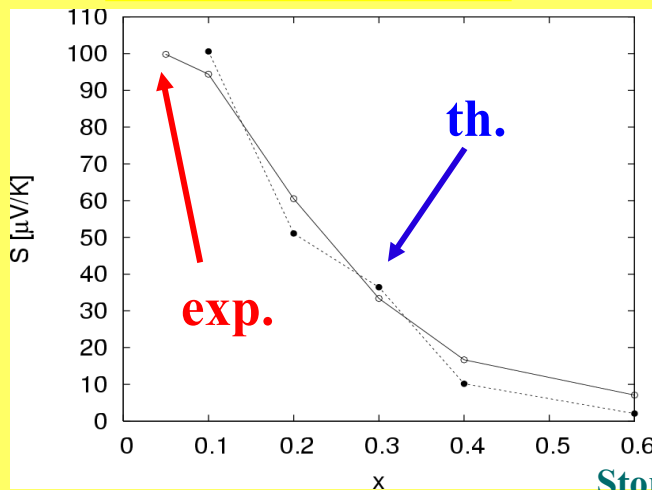
KKR-CPA results

$$\sigma(E) = \frac{2e^2}{3(2\pi)^3\hbar} \int_{\Sigma(E)} dS_{\mathbf{k}} v_{\mathbf{k}} \tau_{\mathbf{k}}$$

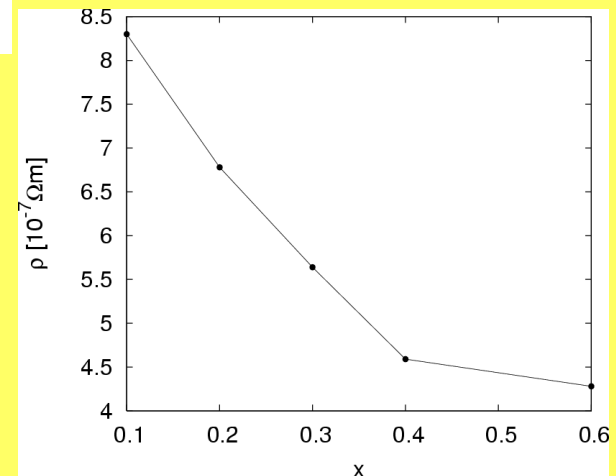
$$S = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \left. \frac{\partial \ln \sigma(E)}{\partial E} \right|_{E_F}$$



$$S_{RT} = (S/T)_0 * 300 \text{ K}$$



Residual resistivity T=0 K



Stopa, Tobola, Kaprzyk, J. Phys. CM (2006)

La₃Cu₃Sb₄

Estimation of thermopower from DOS

$$\sigma(E) = \frac{2e^2}{3(2\pi)^3\hbar} \int_{\Sigma(E)} dS_{\mathbf{k}} v_{\mathbf{k}} \tau_{\mathbf{k}}$$

Residual electrical conductivity

$$S = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \left. \frac{\partial \ln \sigma(E)}{\partial E} \right|_{E_F}$$

Seebeck coefficient

$$S(T) = AT + BT^3 + \dots$$

$$\sigma(E) \sim N_{tot}(E) \mu(E)$$

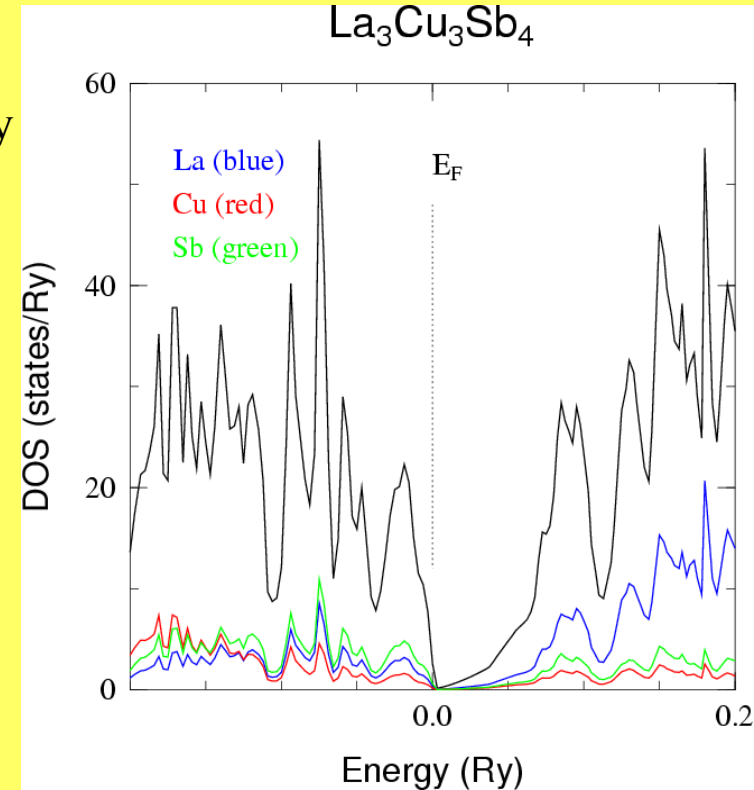
$$S/T \text{ (}\mu\text{V/K}^2\text{)} = 0.2877 \times 10^{-2} \frac{d \ln N_{tot}(E)}{dE}$$

$N_{tot}(E)$ (in states/Ry) at $E=E_F$

Simplified Mott's formula

$$S/T \text{ (}\mu\text{V/K}^2\text{)} = 0.284 \text{ (}\pm 0.1 \text{ !!)}$$

BUT very sensitive to E_F position !!



Temperature	Exper.	Theory
100 K	+38 +20	+28.4
200 K	+72 +39	+56.8
300 K	+100 +63	+85.2

Zamiast podsumowania

The limitations of magnetic refrigeration are only in the minds of the individual engineers or scientists.

Karl Gschneider, 2007

Jednak ograniczenia i problemy **MCE**

Better magnetic refrigerants

Second order magnetic transformation materials with higher MCE

Production of large quantities of magnetic refrigerant

Eventually tons per day

Permanent magnets

Higher strength

Smaller volume

Lower costs

Engineering

Improved designs

Thermodynamic cycles

Improve current AMR cycle

New cycles

First order magnetic transition materials

Fully utilize the structural entropy

Hysteresis

Time dependence

- **5:4 Gadolinium-Silicon-Germanium**
 - $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$
- **Manganites**
 - $(\text{R}_{1-x}\text{M}_x)\text{MnO}_3$
 - R - Lanthanide, M – Alkali, Alkaline earth
- **Lanthanum-Iron-Silicon**
 - $\text{R}(\text{Fe}_{1-x}\text{Si}_x)_{13}$
- **Manganese-Antimony Arsenide**
 - $\text{MnAs}_{1-x}\text{Sb}_x$
- **Iron-Manganese-Arsenic Phosphides**
 - $(\text{FeMn})(\text{P}_{1-x}\text{As}_x)$
- **Heusler Alloys**
 - $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$
- **Gadolinium - Benchmark Material**

Współpraca



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Podziękowania za materiały:

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11. - 13. April 2007, Portoroz, Slovenia

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