Universidade Federal do ABC

Grupo de Materiais Quânticos

Simplicity vs. complexity in thermoelectric quantum materials: the cases of $FeGa_3$ and RT_2Zn_{20}

Marcos A. Avila

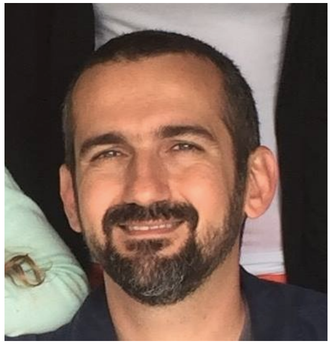
UFABC Collaborators

Michael Cabrera

Raquel Ribeiro

Carlos Rettori

Camilo Alvarez



Gustavo Dalpian

Jorge Osorio

Other Collaborators

Hiroshima University

Magnetism and Thermoelectrics
K. Suekuni, T. Takabatake

High Pressures, ^{3}He Temperatures
K. Umeo

Single Crystal XRD
H. Fukuoka, S. Yamanaka

Raman Scattering
Y. Takasu, M. Udagawa

Ultrasound Attenuation
I. Ishii, T. Suzuki

SEM, TEM
T. Ekino

XPS, XANES, RXES
H. Sato, K. Shimada, Y. Takahashi

Other Institutions

EXAFS
F. Bridges (UCSD - San Diego)

XPS
K. Tanigaki (Tohoku U. - Sendai)

Inelastic Neutron Scattering
C. H. Lee (AIST - Tsukuba)

THz Optical Conductivity
T. Mori, N. Toyota (Tohoku U. - Sendai)

Neutron Diffraction
M. Christensen (Aarhus U. - Denmark)

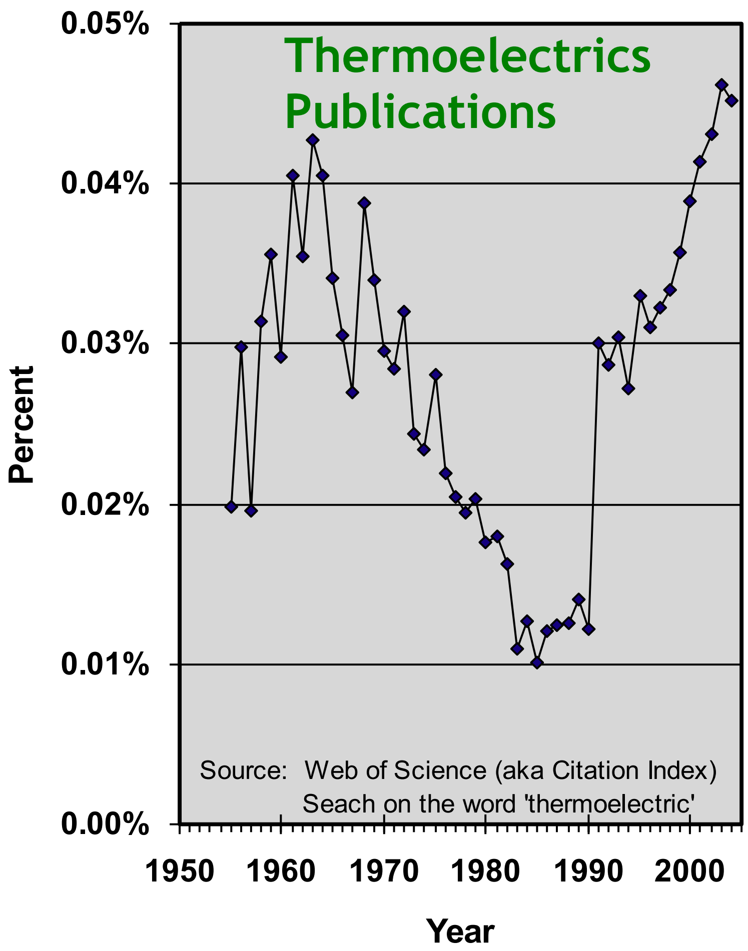
Mössbauer
E. Baggio-Saitovitch, J. Munevar (CBPF)

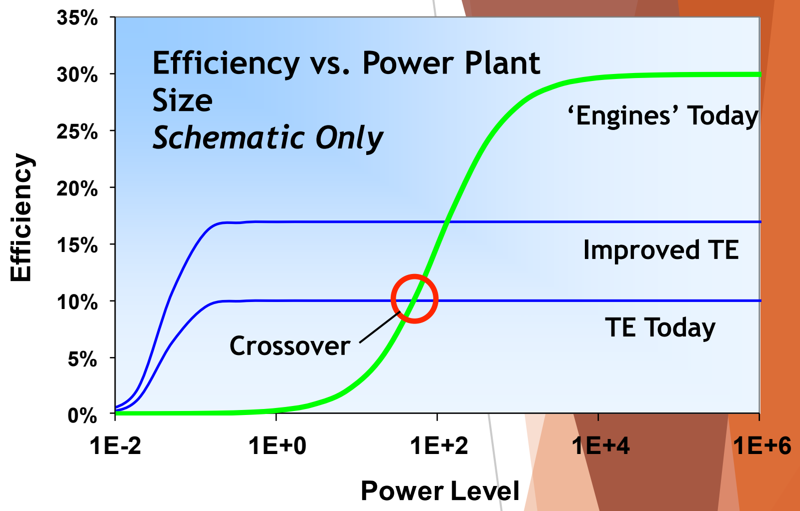
XRD, XPS, XANES, XMCD
C. Giles (UNICAMP), D. Haskel (APS)

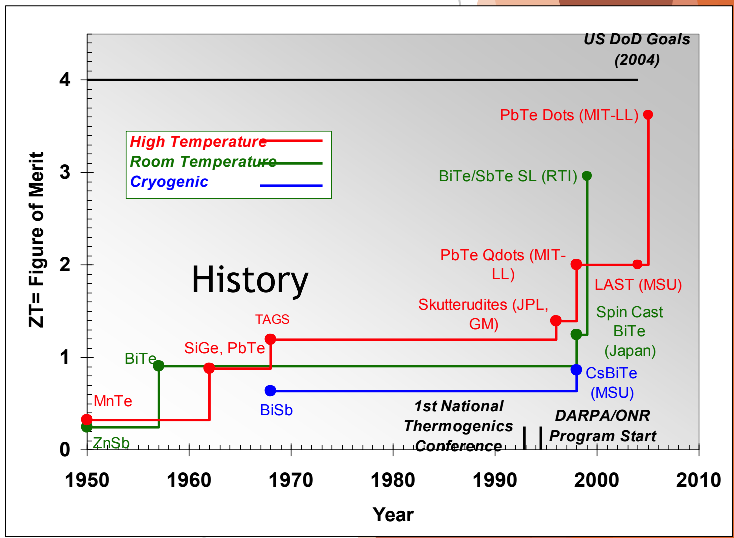
Outline

- Materials Research for Thermoelectrics
  - Thermoelectric Devices
  - Thermoelectric Conversion Efficiency
  - Next Generation Thermoelectric Materials
- Thermoelectricity and Magnetism in $FeGa_3$
  - Experiments and DFT simulations
- Electronic Structure and Magnetism in RT_2Zn_{20}
  - Experiments and DFT simulations

Thermoelectrics Ressurgence







C. Vining, *ECT* 2008

Thermoelectric Devices

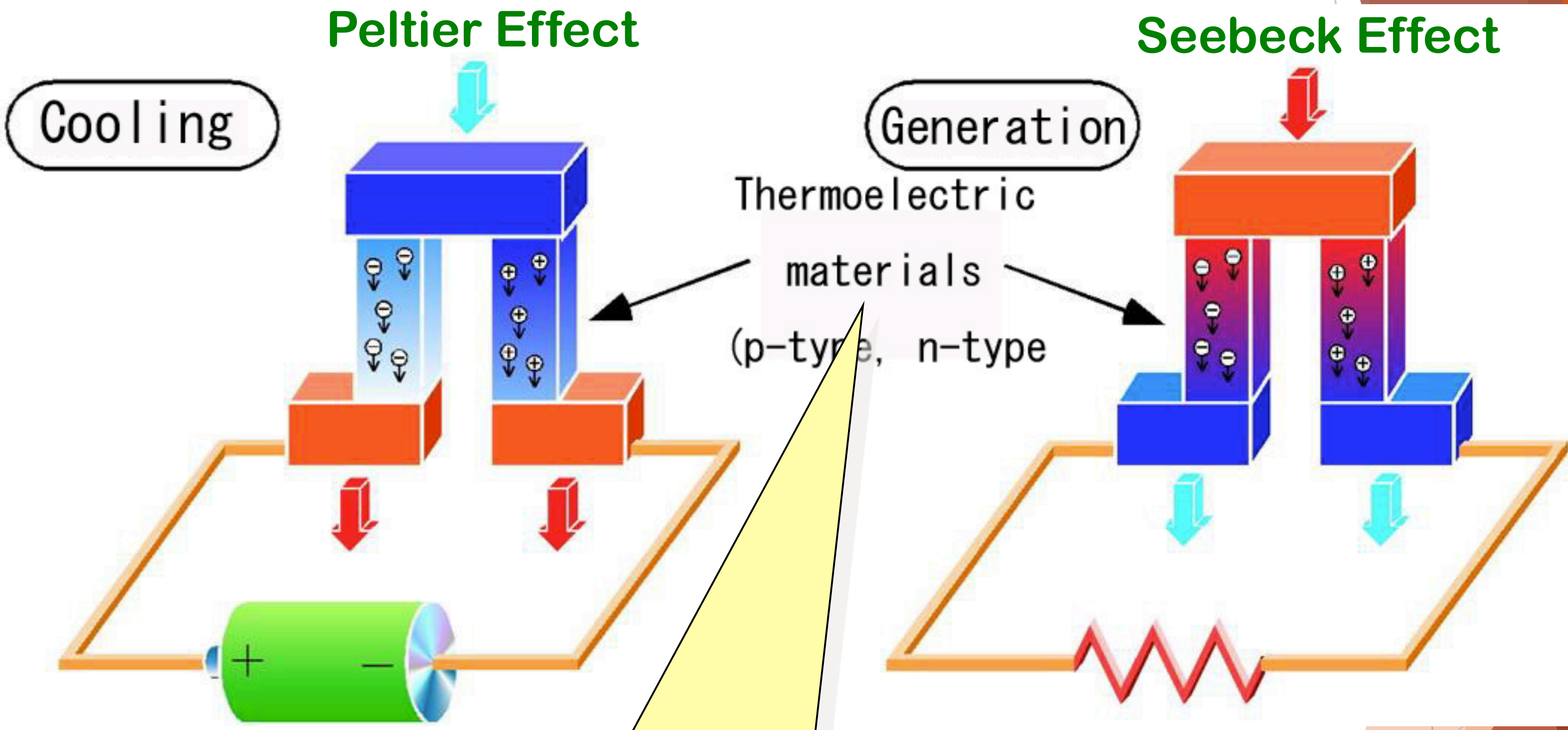


image: www.jaist.ac.jp

Basic Material Requirements:
p- & n-type | high S | low ρ | low κ

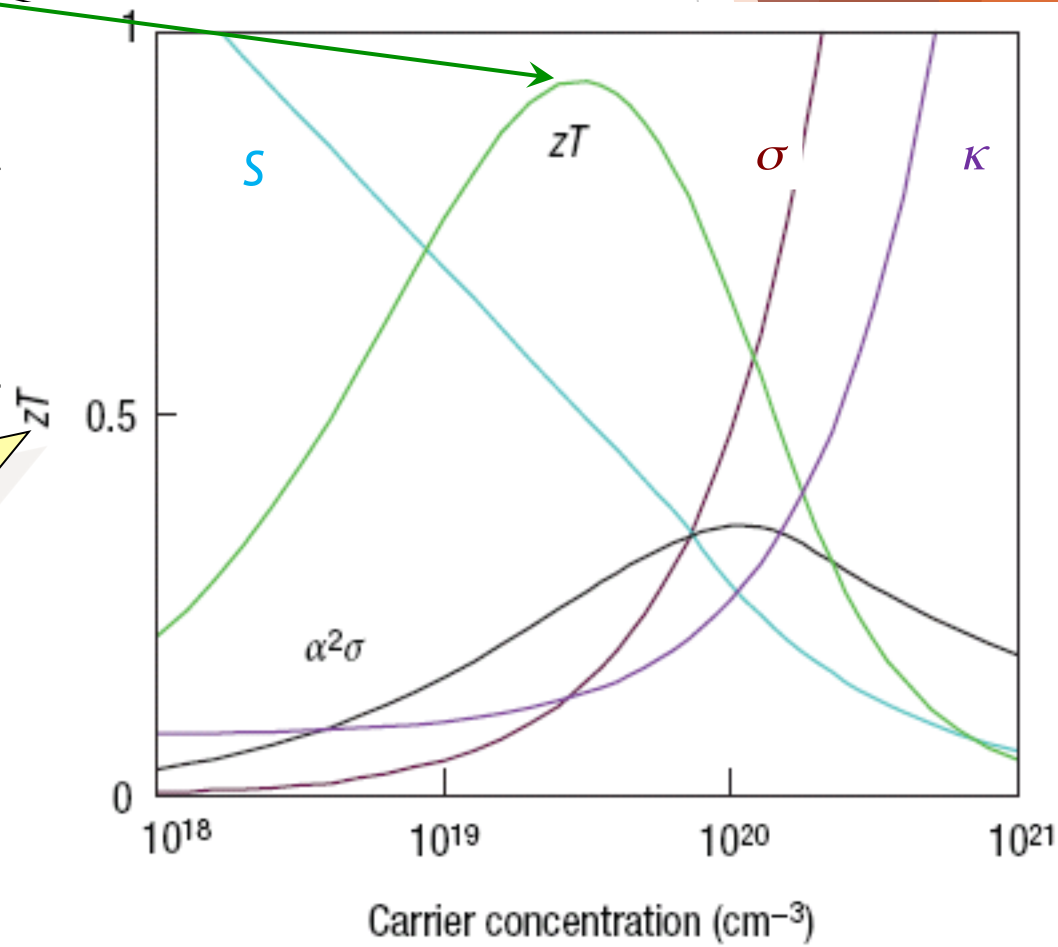
- Free & renewable energy;
- Waste heat recovery;
- Environmentally friendly.

Conversion Efficiency

TE Figure of Merit:

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

Electron Transport Theory
(single parabolic band)



Common Metals

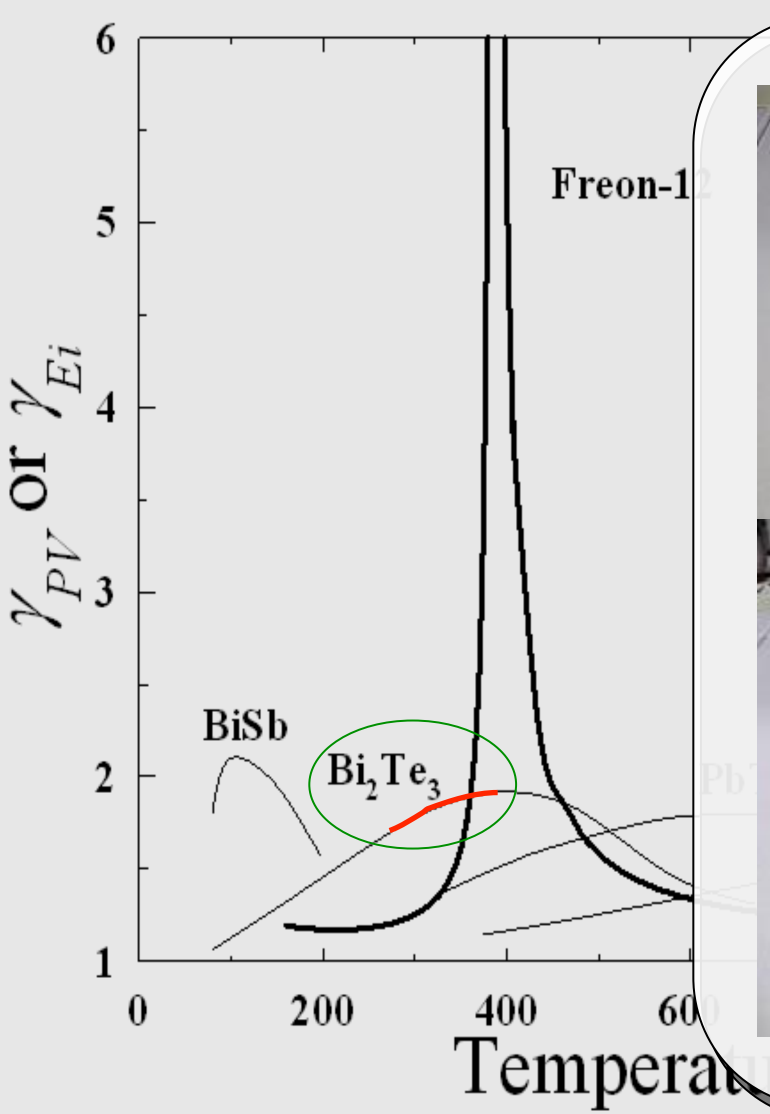
$ZT \cong 10^{-4} - 10^{-2}$

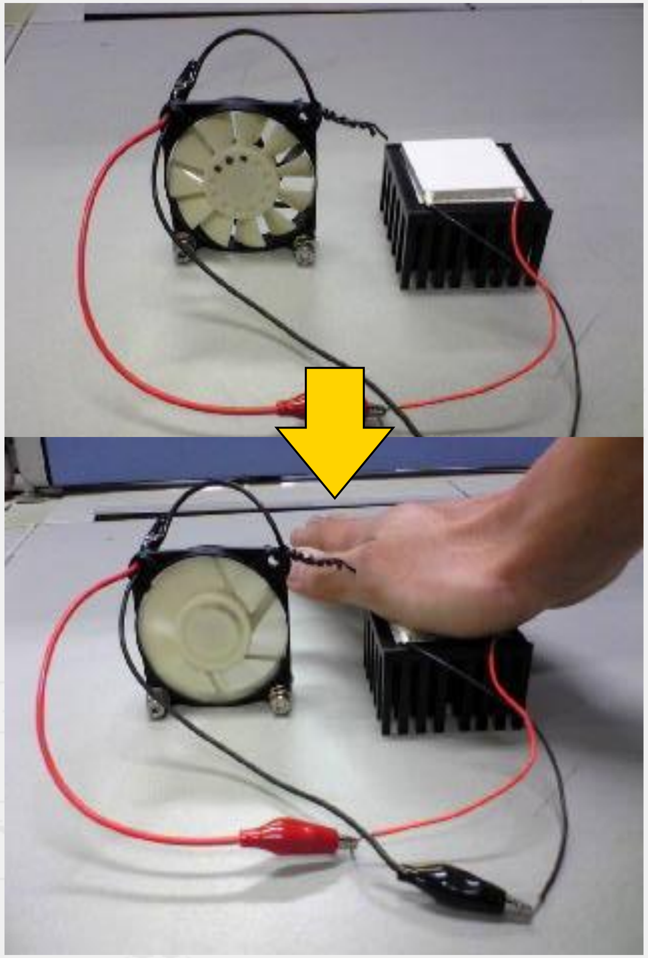
Best Materials

$ZT \cong 1$

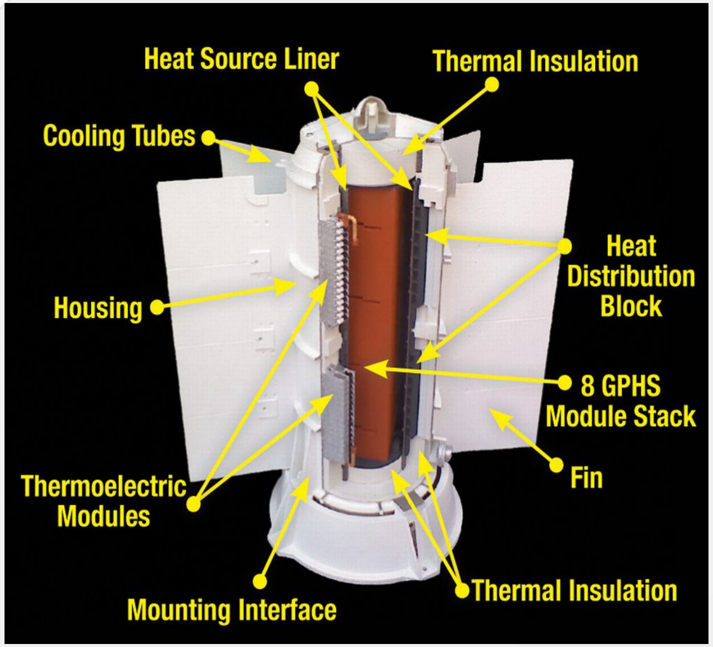
(~10% efficiency)

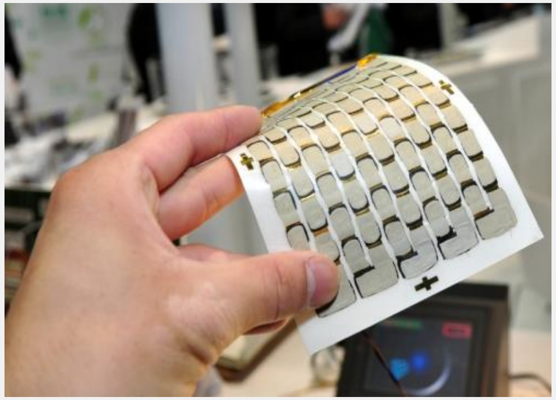
Classic Materials





Application Examples





New Materials Research

80's | Enhance S through **strongly correlated electrons**

90's | **Heavy Fermions, Kondo Semiconductors…**

Find compounds with **new/exotic mechanisms** that may allow some degree of independence between S, ρ and κ

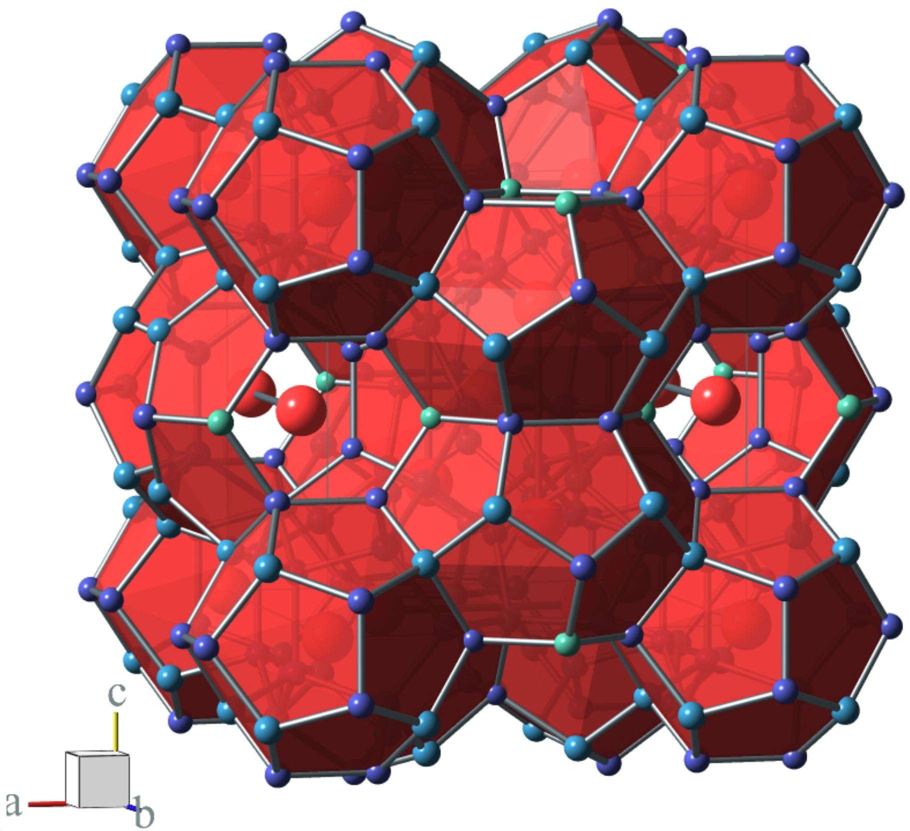
$$\frac{S^2}{\rho \cdot (\kappa_L + \kappa_{el})} T$$

90's | Reduce loss factors ρ and κ. **Slack (1995):**

00's | $\Rightarrow$ ***"Phonon Glass, Electron Crystals"* (PGEC)**

β-$Ba_8Ga_{16}Sn_{30}$ Structure

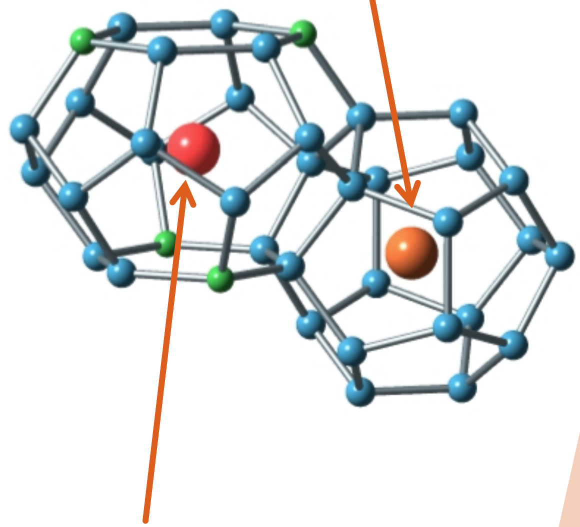
Unit cell (54 atoms: A_8X_{46})



Cubic *Pm*3*n* (#223); *a* ~ 1.2 nm

2×Ba1 (2*a*) - bcc

Dodecahedron (X_{20})

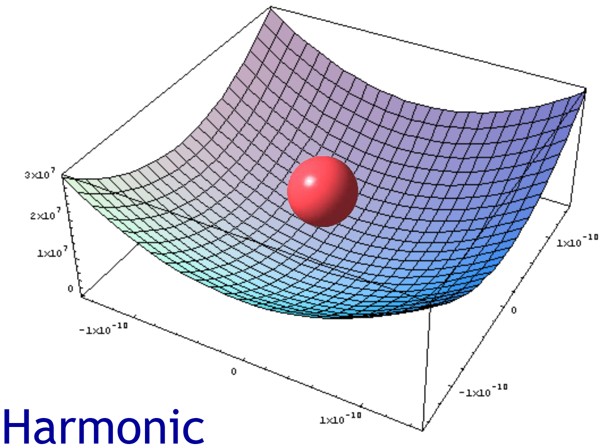


6×Ba2 (6*d*) – "fcc"

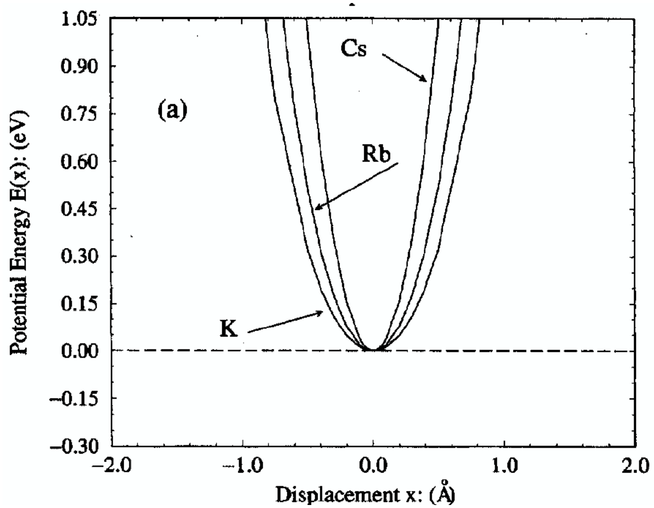
Tetrakaidecahedron (X_{24})

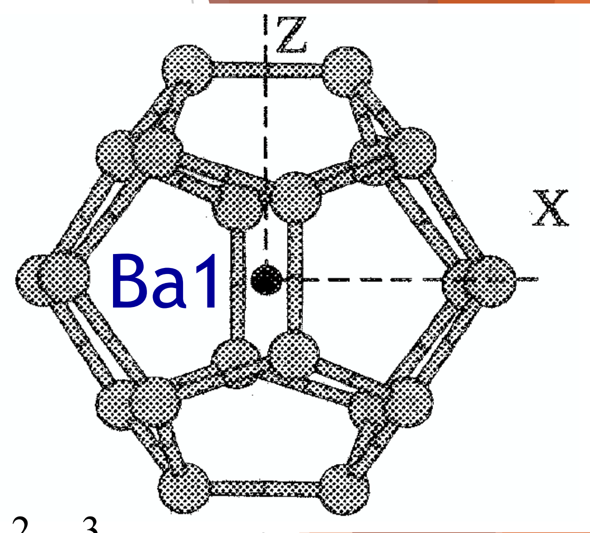
β-BGS Off-Center Rattling

On-center

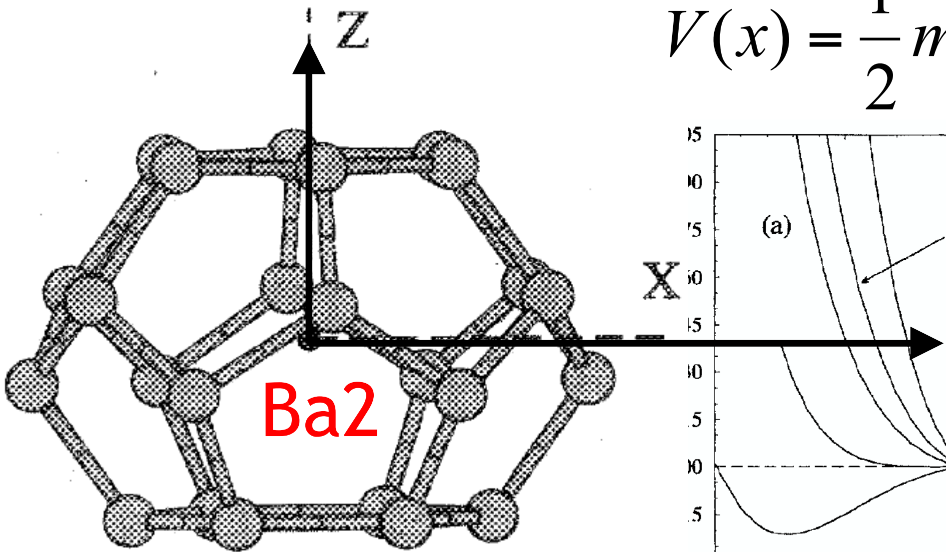


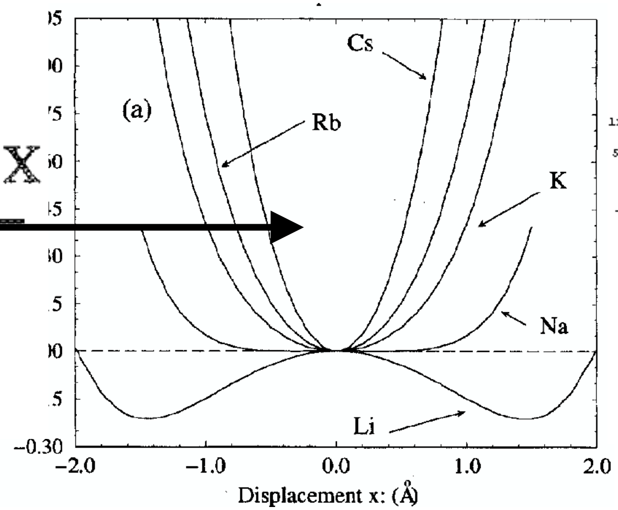
Harmonic



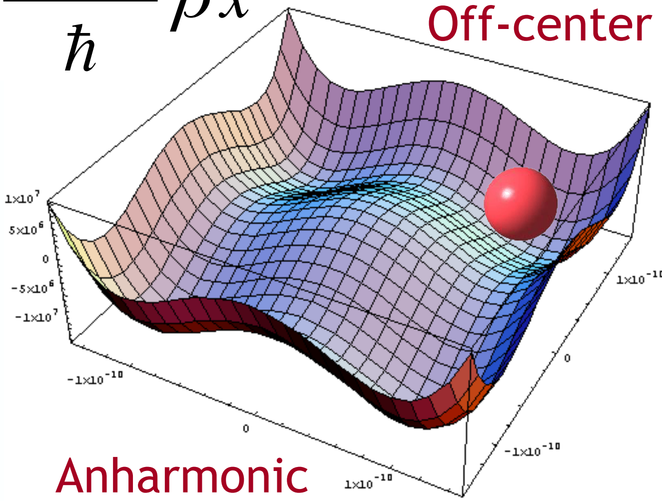


$$V(x) = \frac{1}{2} m\omega^2 \alpha x^2 + \frac{1}{2} \frac{m^2\omega^3}{\hbar} \beta x^4$$



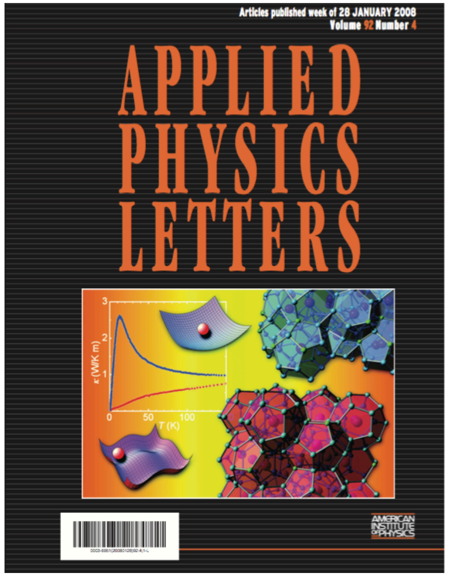


Off-center



Anharmonic

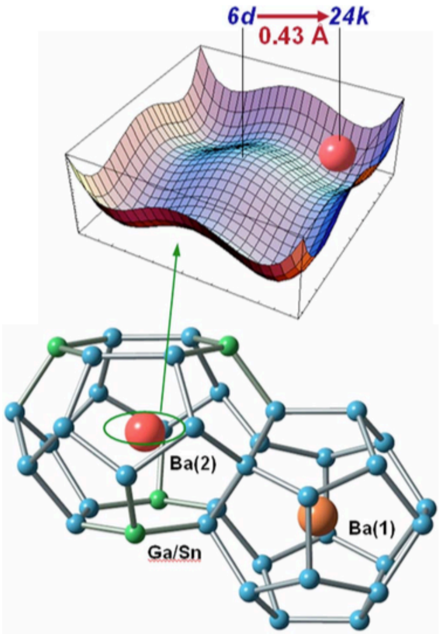
β-BGS Off-Center Rattling

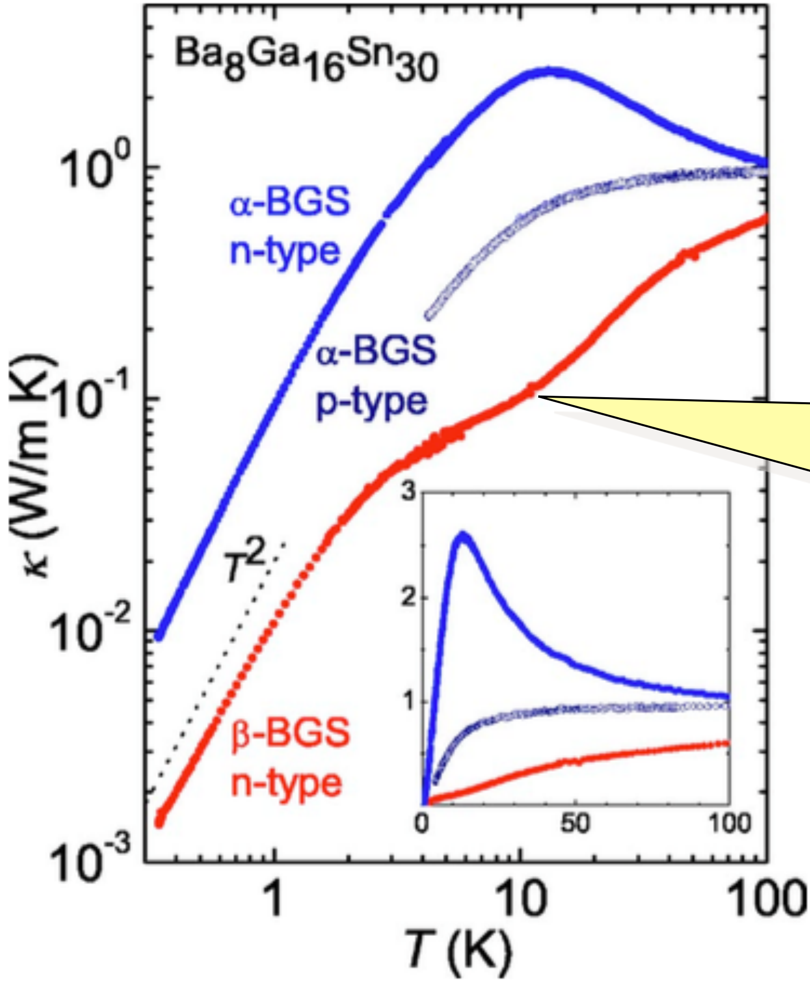


APPLIED PHYSICS LETTERS **92**, 041901 (2008)

$Ba_8Ga_{16}Sn_{30}$ with type-I clathrate structure: Drastic suppression of heat conduction

M. A. Avila,[1,a)] K. Suekuni,[1] K. Umeo,[2] H. Fukuoka,[3] S. Yamanaka,[3] and T. Takabatake[1,4]





Lowest κ(T) of all type-1 clathrates

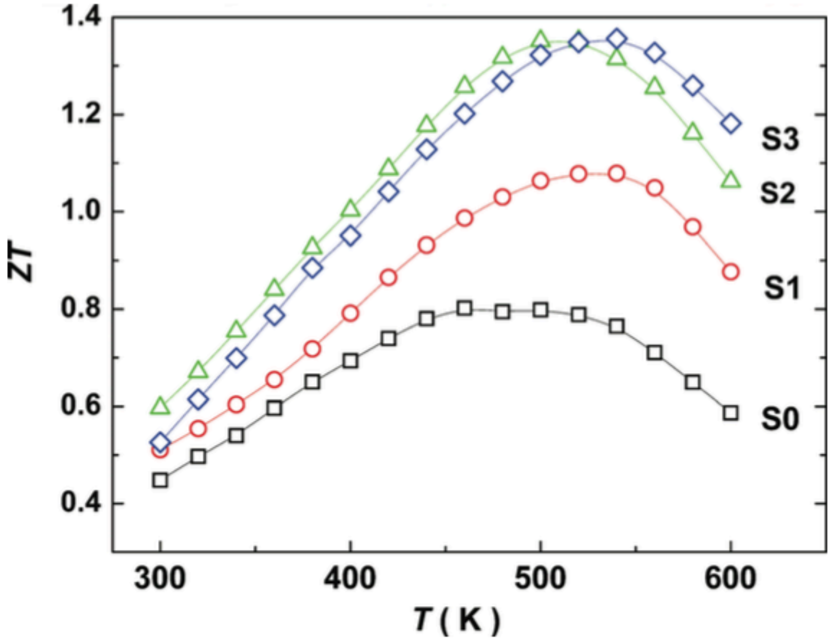
Comparable to amorphous silica glass (a-SiO_2)!

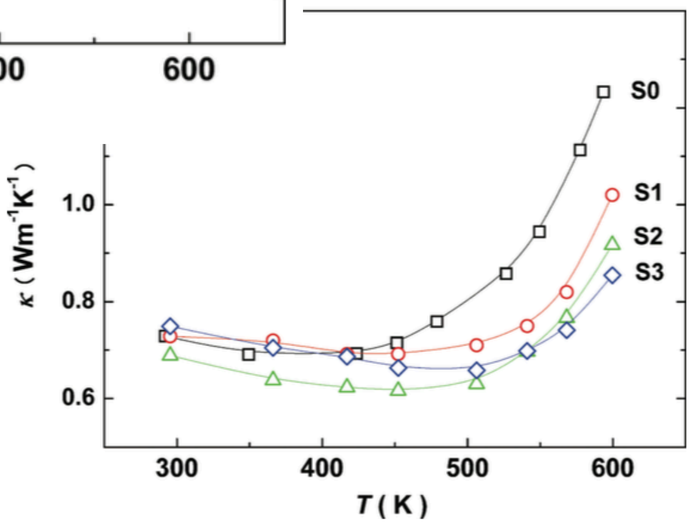
β-BGS Off-Center Rattling

JOURNAL OF APPLIED PHYSICS **109**, 103704 (2011)

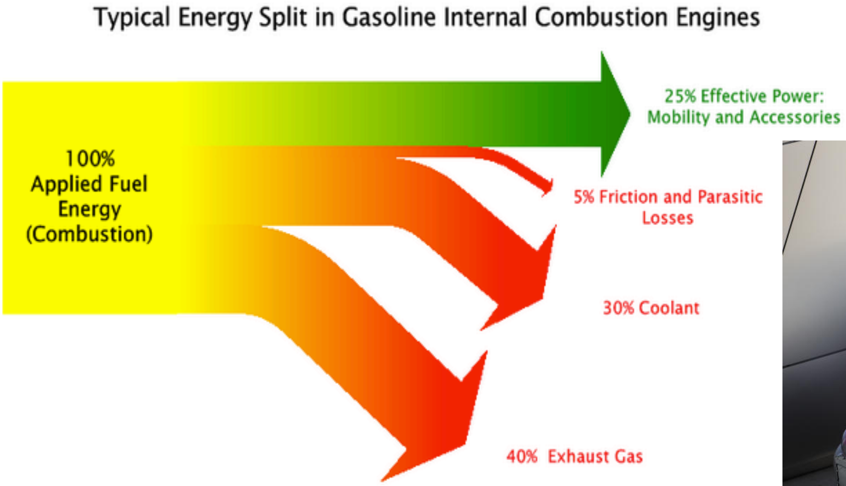
High thermoelectric performance of Cu substituted type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$ single crystals

Shukang Deng,[1,2] Yuta Saiga,[1] Kousuke Kajisa,[1] and Toshiro Takabatake[1,a)]





Can TE go “mainstream”?

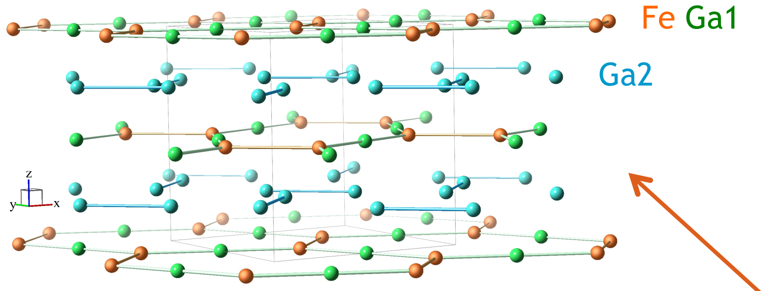


Automotive
Coolant and Exhaust
Heat Recovery

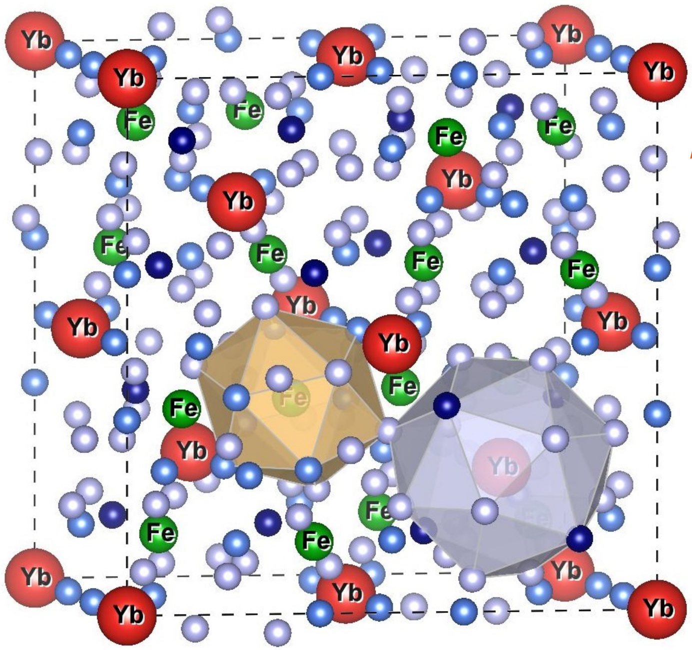
$ZT = 0.5 – 1.0$
is acceptable, if
device is low cost
and light weight

Cases at Hand

- $FeGa_3$ (layer structure)



- RT_2Zn_{20} (cage structure)



Unit cell:
184 atoms
a ~ 1.5 nm

Nicely tractable model system

Nightmare to understand and model the physics

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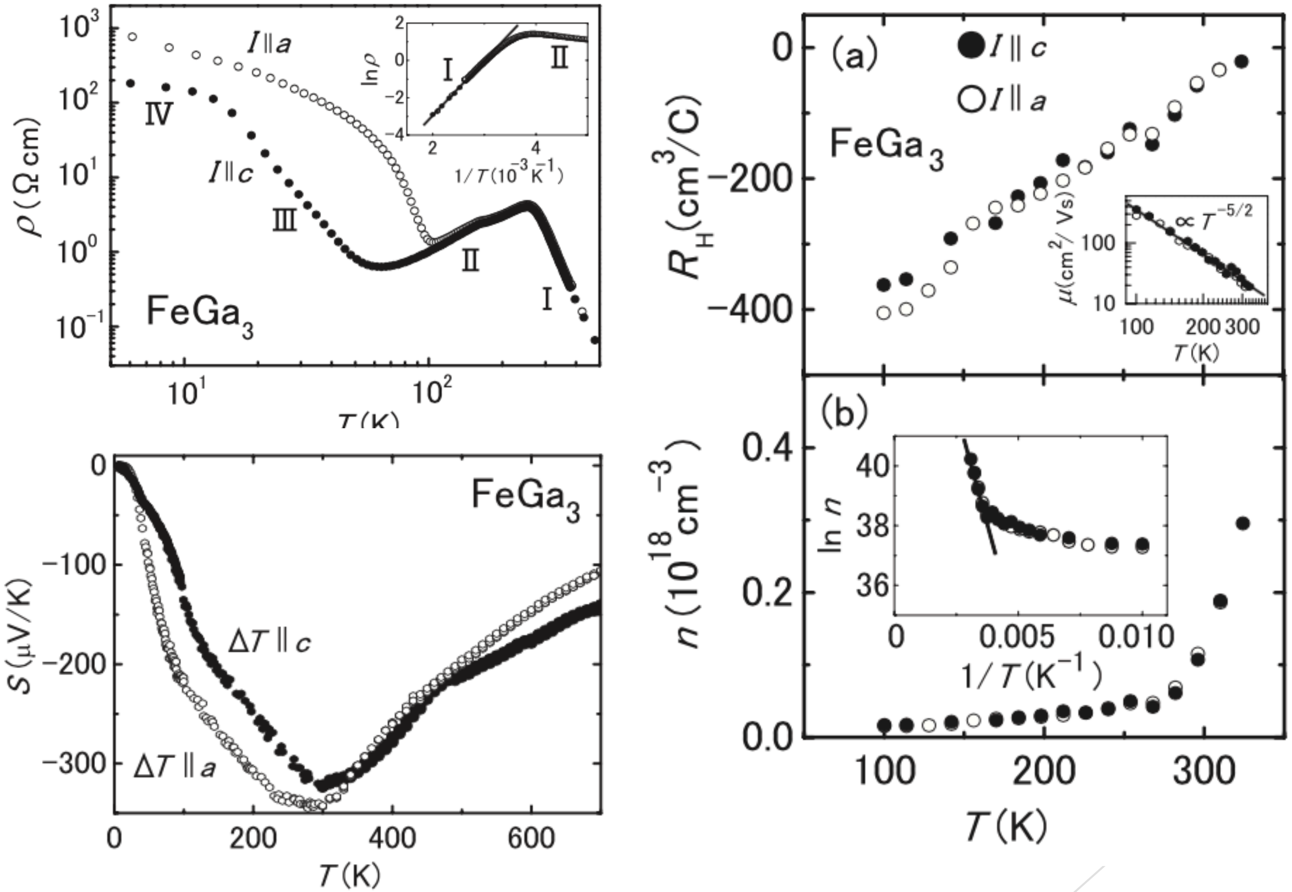
Binary Semiconductor $FeGa_3$

Journal of the Physical Society of Japan
Vol. 78, No. 1, January, 2009, 013702

Thermoelectric and Magnetic Properties of a Narrow-Gap Semiconductor $FeGa_3$

Yuta HADANO[1], Shouta NARAZU[1], Marcos A. AVILA[1],
Takahiro ONIMARU[1], and Toshiro TAKABATAKE[1,2*]

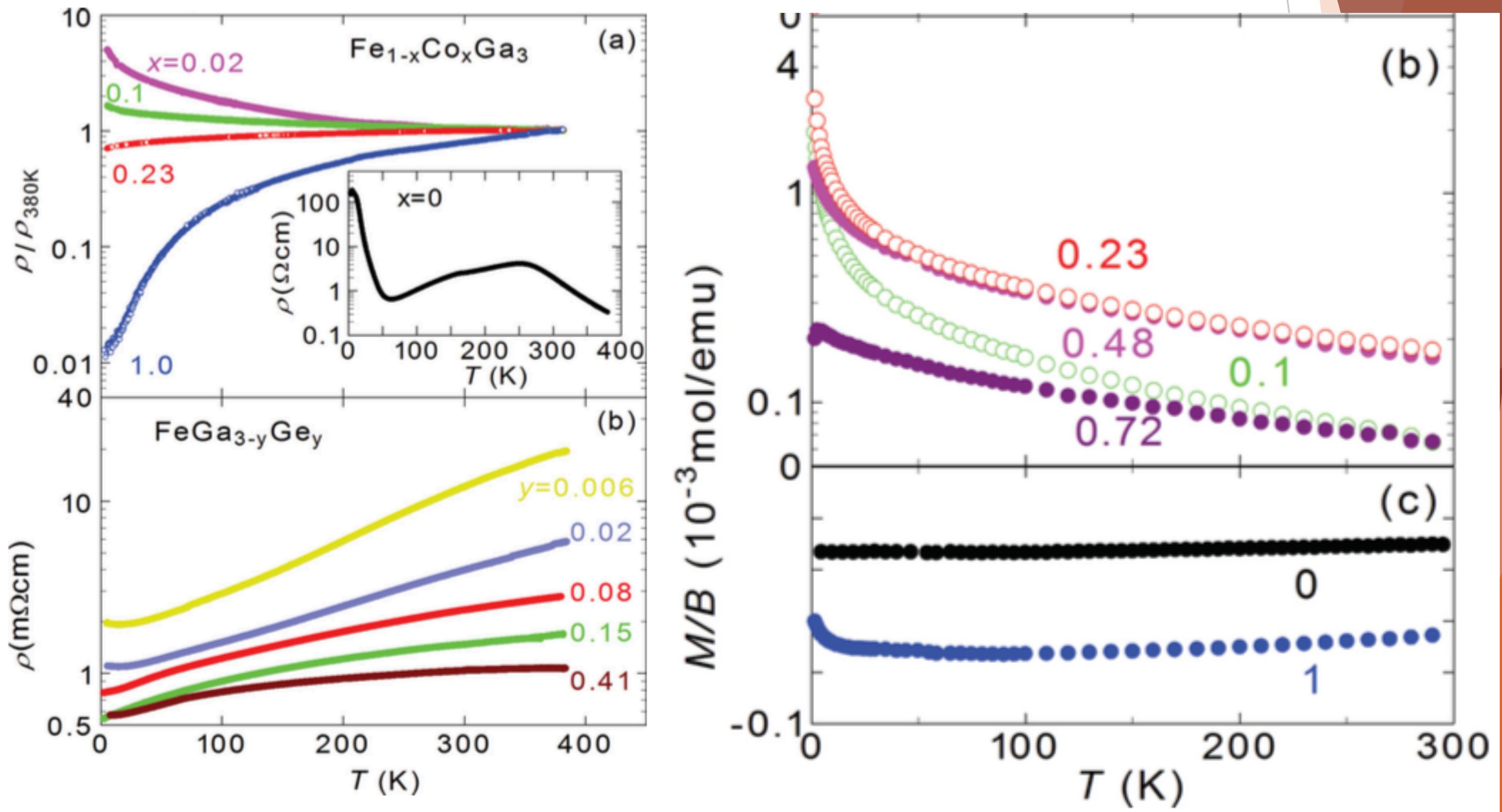


Electron-doped $FeGa_3$

PHYSICAL REVIEW B **86**, 144421 (2012)

Ferromagnetic instability in a doped band gap semiconductor $FeGa_3$

K. Umeo,[1,2,*] Y. Hadano,[2] S. Narazu,[2] T. Onimaru,[2] M. A. Avila,[3] and T. Takabatake[2,4]



$FeGa_{3-x}Ge_x$: New Quantum Material

PHYSICAL REVIEW B **86**, 144421 (2012)

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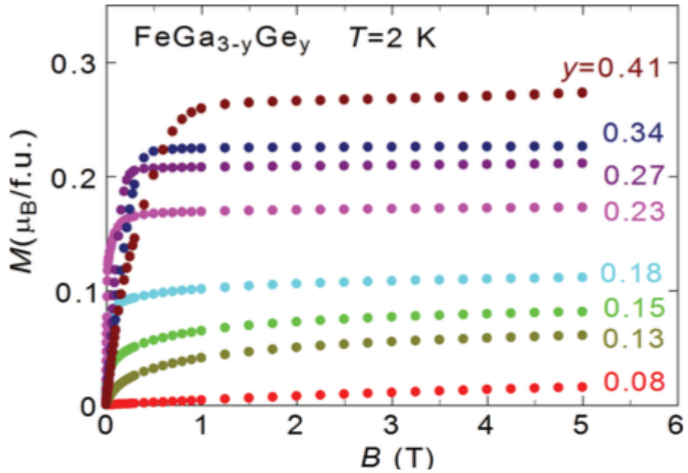
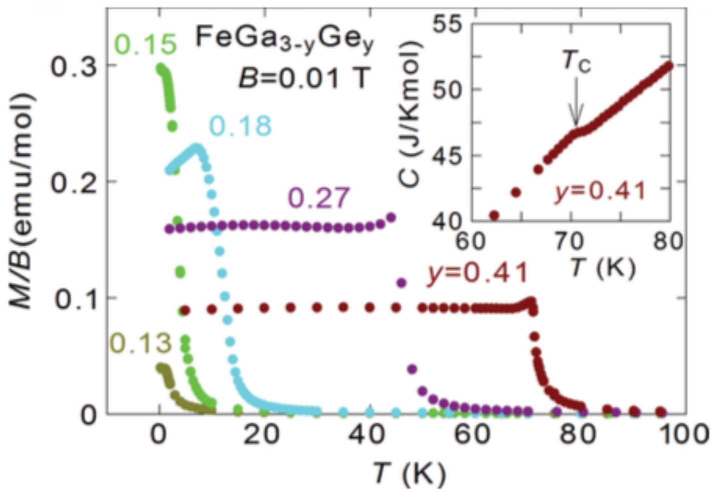
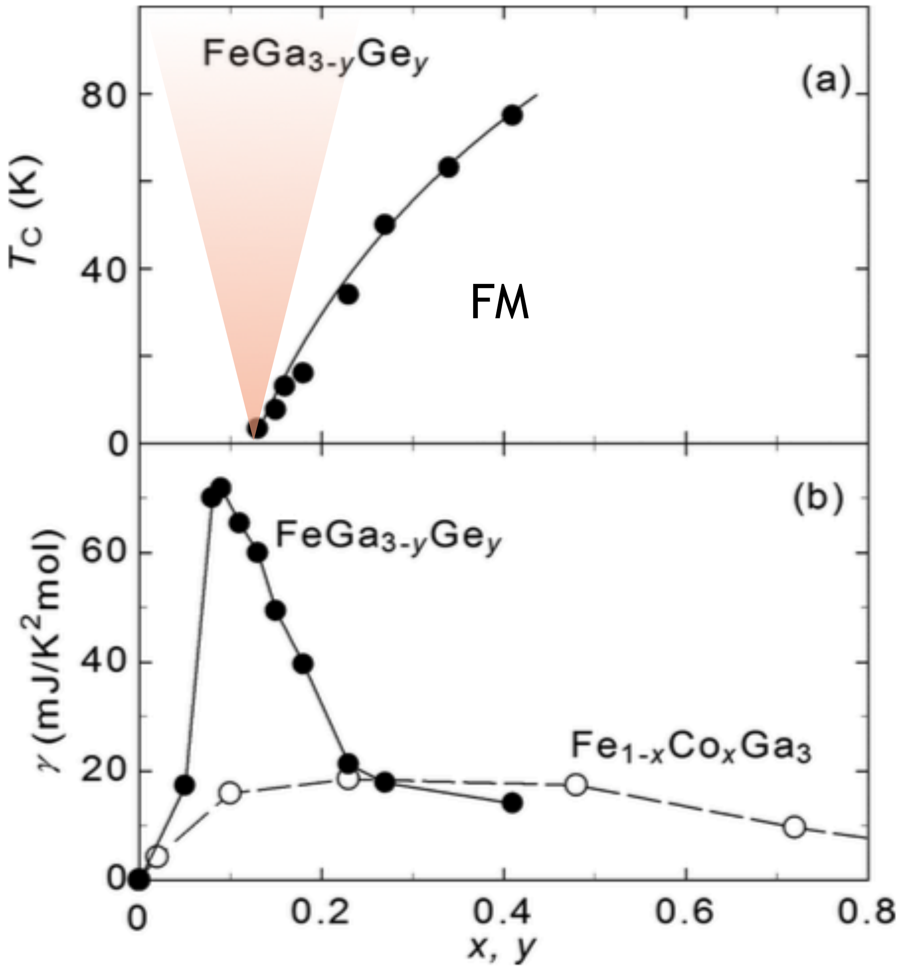






$FeGa_{3-x}Ge_x$: New Quantum Material

PHYSICAL REVIEW B **82**, 155202 (2010)

Evidence for a spin singlet state in the intermetallic semiconductor $FeGa_3$

PHYSICAL REVIEW B **86**, 235202 (2012)

Pressure-induced metal-insulator transition and absence of magnetic order in $FeGa_3$ from a first-principles study

J. M. Osorio-Guillén*
Instituto de Física, Universidad de Antioquia, Medellín, Colombia and Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil

Y. D. Larrauri-Pizarro and G. M. Dalpian
Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil
(Received 13 September 2012; published 3 December 2012)

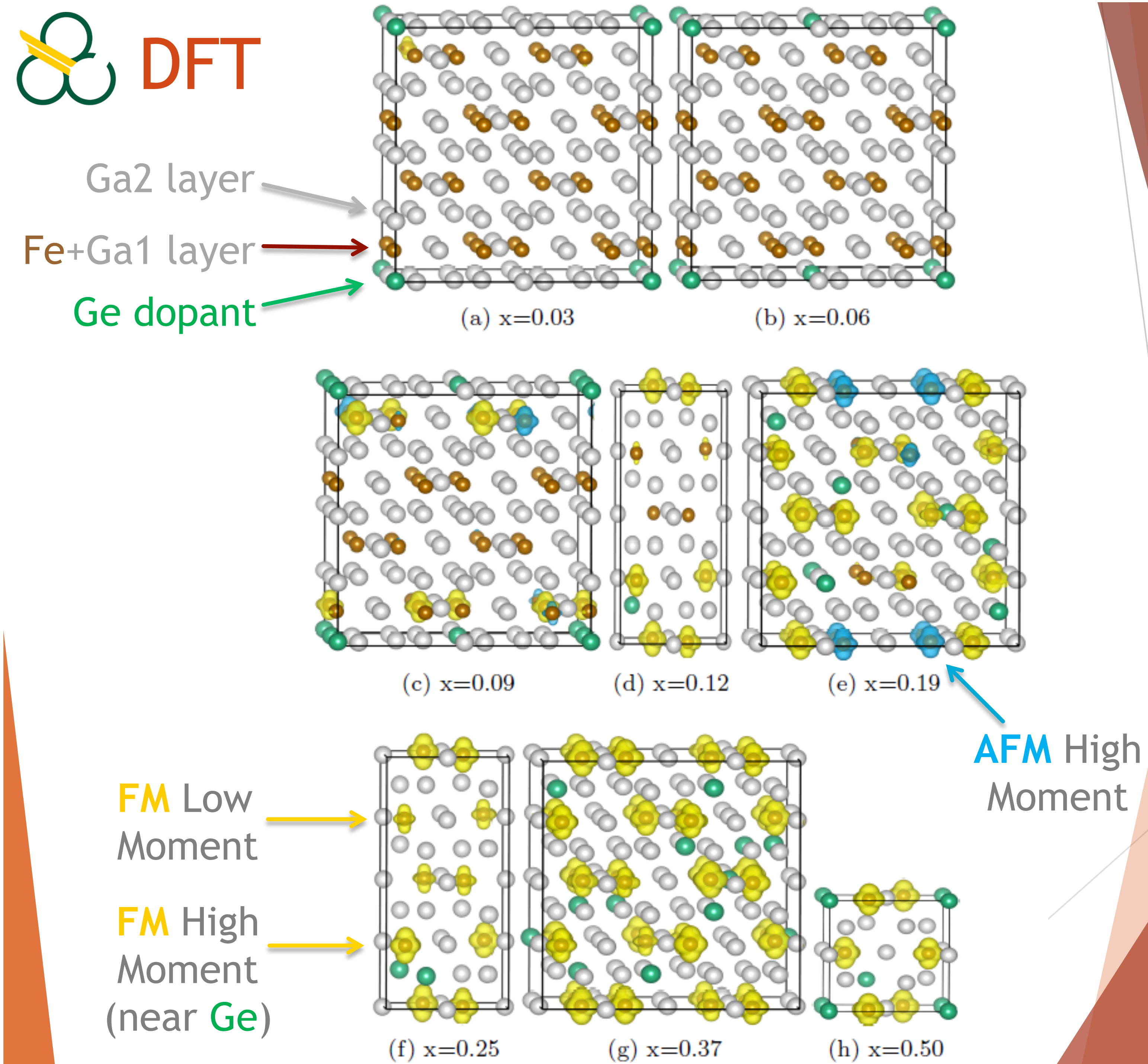
PHYSICAL REVIEW B **88**, 064422 (2013)

Itinerant origin of the ferromagnetic quantum critical point in $Fe(Ga,Ge)_3$

PHYSICAL REVIEW B **89**, 104426 (2014)

Interplay between localized and itinerant magnetism in Co-substituted $FeGa_3$

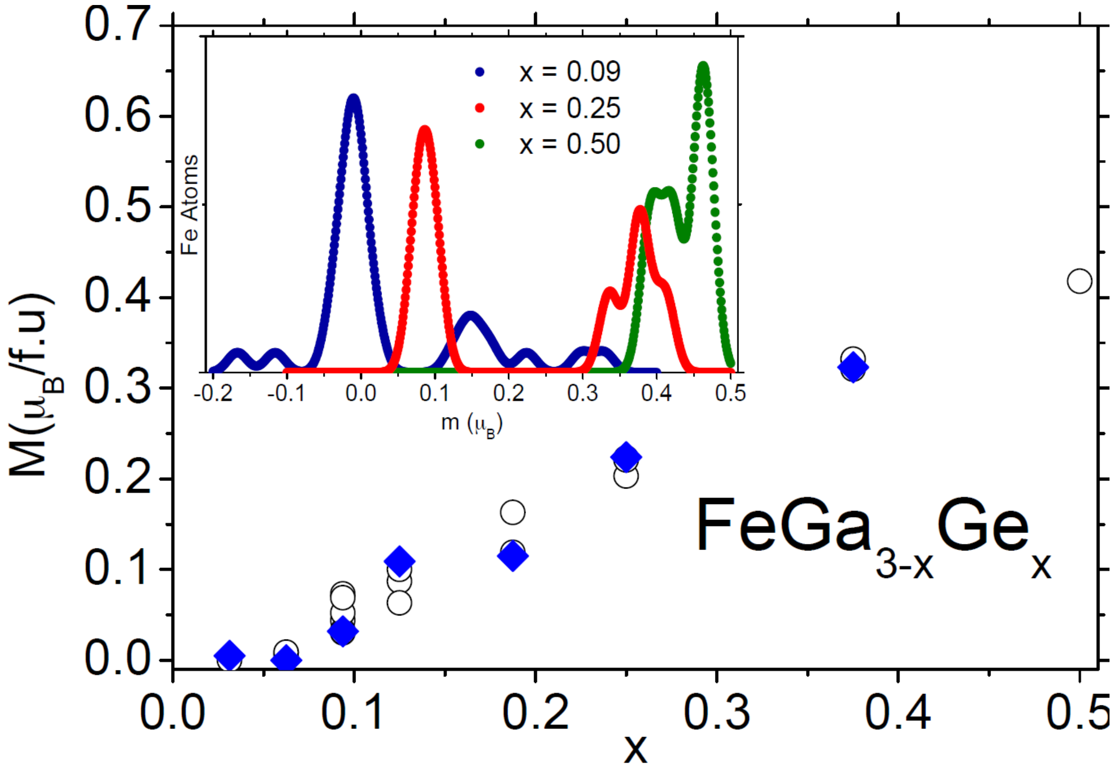
DFT


Ga2 layer
Fe+Ga1 layer
Ge dopant
(a) x=0.03
(b) x=0.06
(c) x=0.09
(d) x=0.12
(e) x=0.19
AFM High Moment
FM Low Moment
FM High Moment (near Ge)
(f) x=0.25
(g) x=0.37
(h) x=0.50

DFT

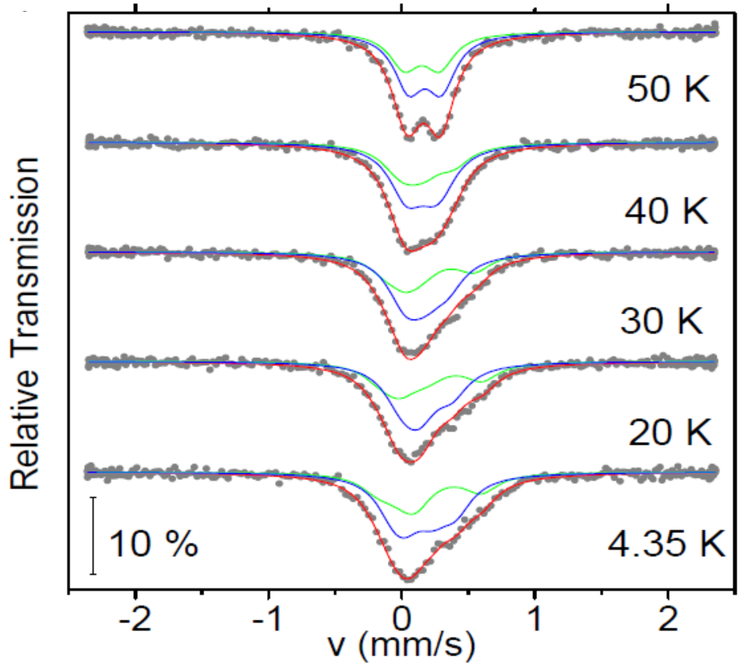
Emergence of competing magnetic interactions induced by Ge doping in the semiconductor FeGa3

J. C. Alvarez-Quiceno, M. Cabrera-Baez, R. A. Ribeiro, M. A. Avila,* and G. M. Dalpian†
J. M. Osorio-Guillén‡

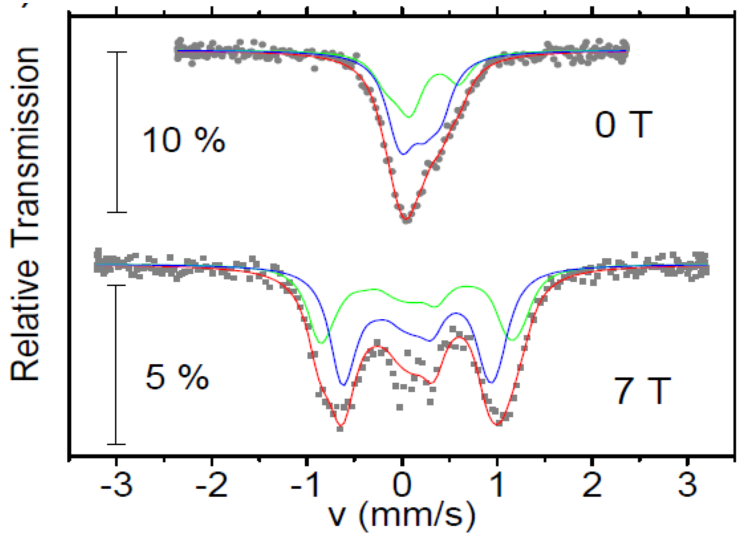


Evolution from **localized** towards **itinerant** magnetism with increasing Ge content

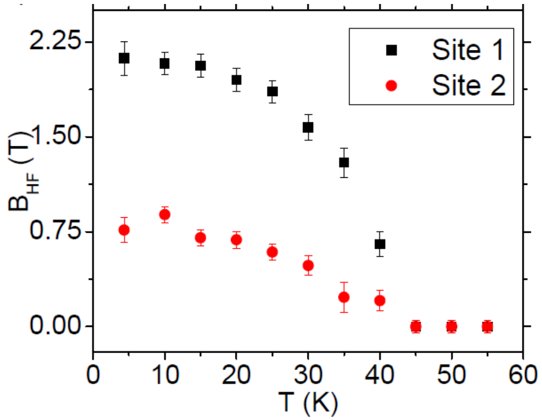
Mössbauer



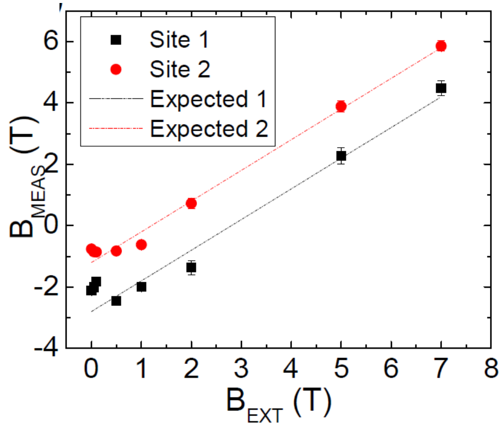
Relative Transmission
50 K
40 K
30 K
20 K
4.35 K
10 %
-2
-1
0
1
2
v (mm/s)



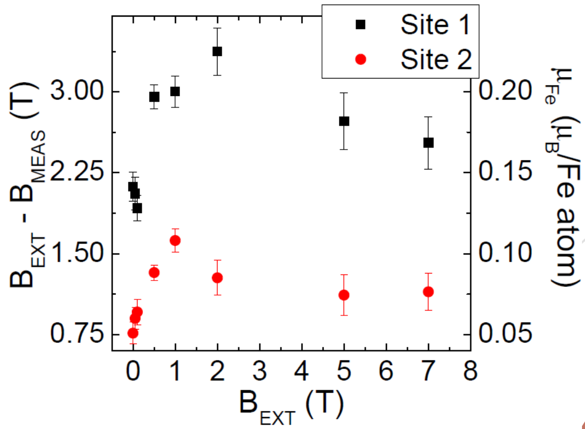
Relative Transmission
10 %
0 T
5 %
7 T
-3
-2
-1
0
1
2
3
v (mm/s)



Site 1
Site 2
2.25
1.50
0.75
0.00
B_HF (T)
0
10
20
30
40
50
60
T (K)

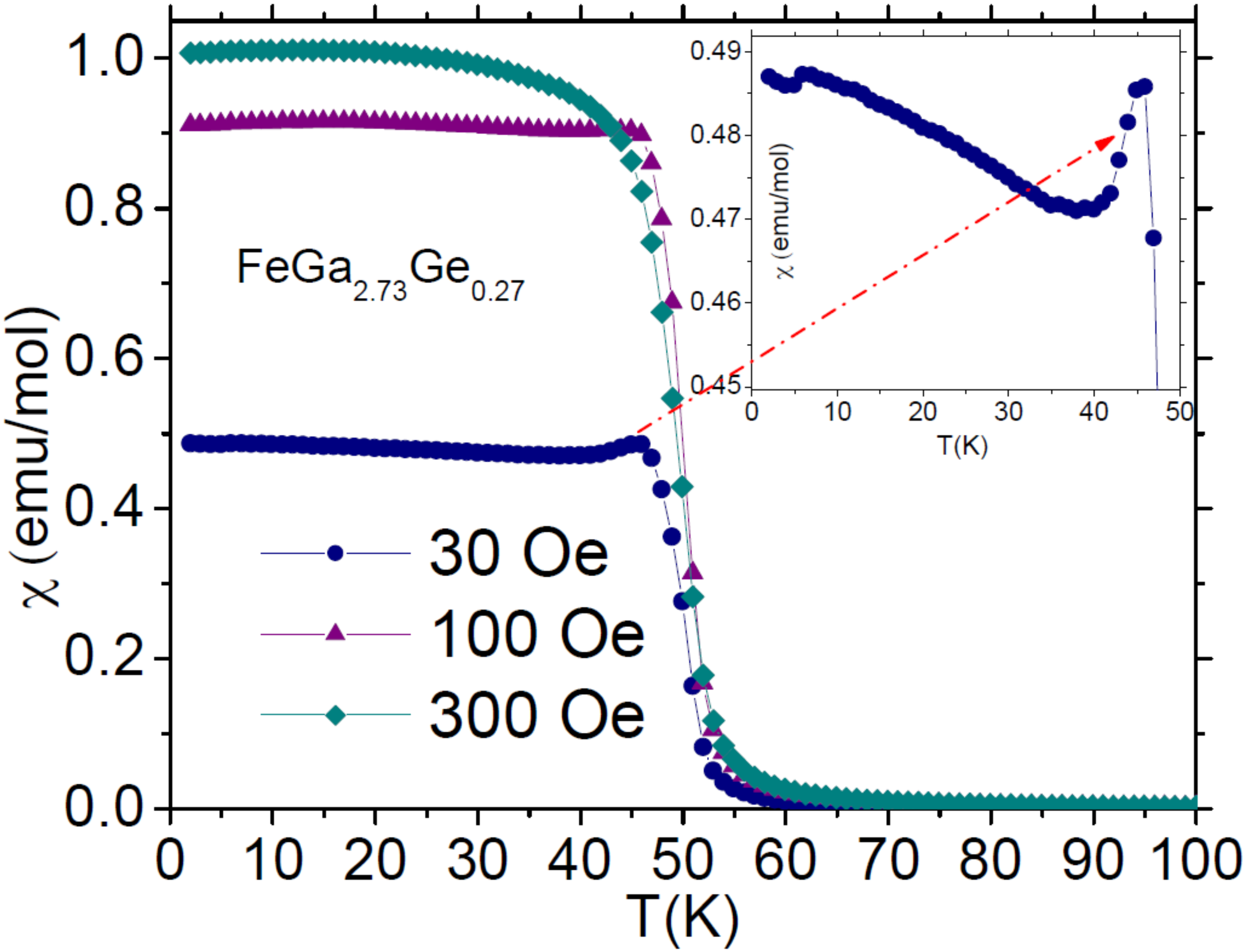


Site 1
Site 2
Expected 1
Expected 2
6
4
2
0
-2
-4
B_MEAS (T)
0
1
2
3
4
5
6
7
8
B_EXT (T)



Site 1
Site 2
3.00
2.25
1.50
0.75
B_EXT - B_MEAS (T)
0.20
0.15
0.10
0.05
μ_Fe (μ_B/Fe atom)
0
1
2
3
4
5
6
7
8
B_EXT (T)

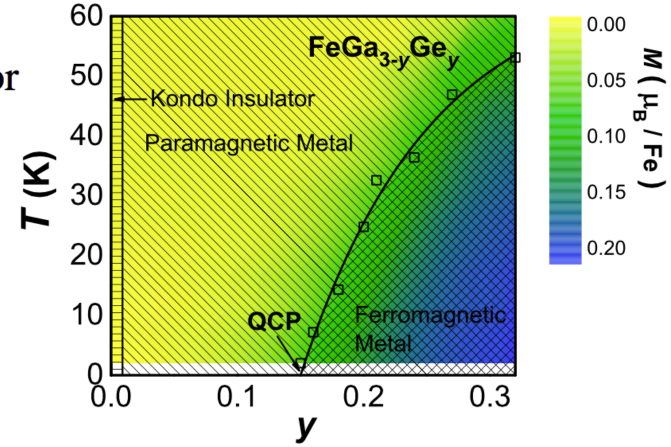
Magnetization

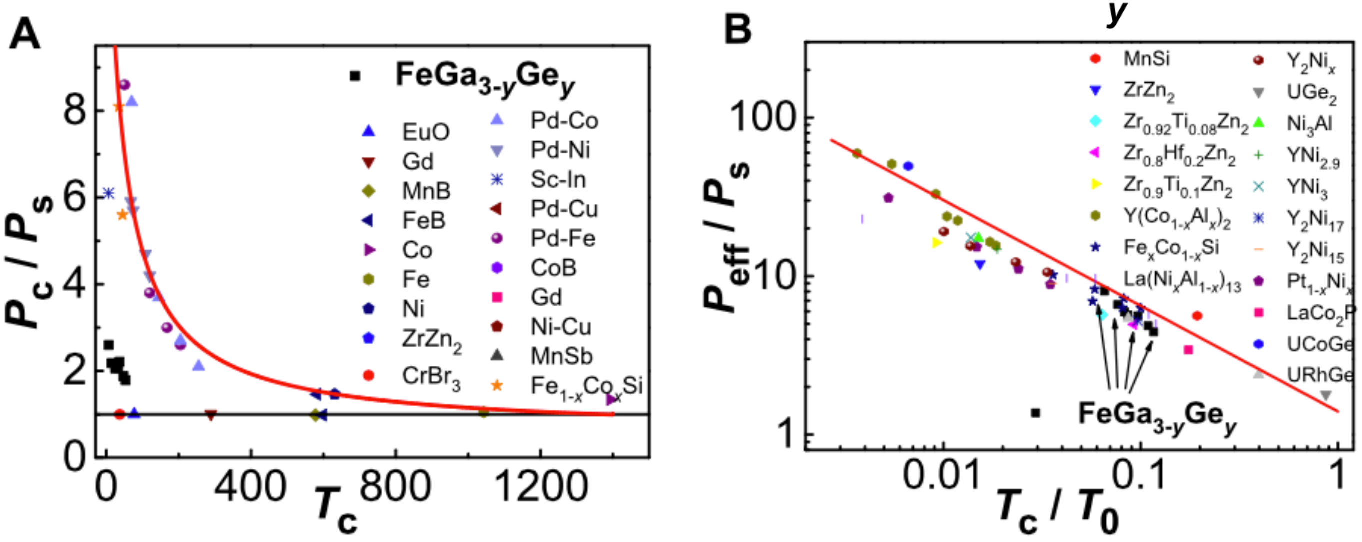


Magnetization

Transitions from a Kondo-like diamagnetic insulator into a modulated ferromagnetic metal

Yao Zhang,[1*] Masaki Imai,[1] Chishiro Michioka,[1] Yuta Hadano,[2]
Marcos A. Avila,[3] Toshiro Takabatake,[2] Kazuyoshi Yoshimura,[1,4†]





Rhodes-Wohlfarth plot and Deguchi-Takahashi plot.

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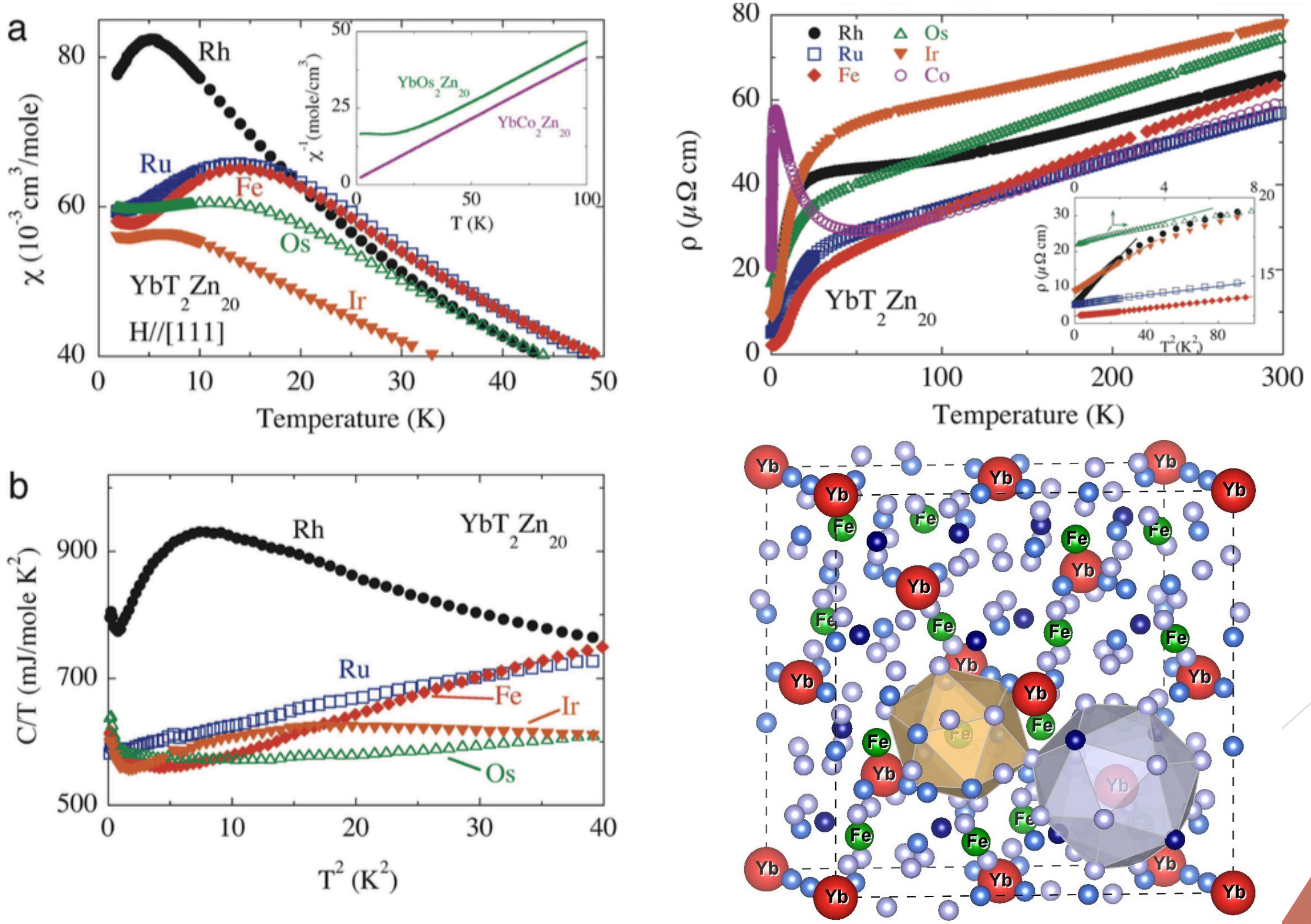
Cage Compounds RT_2Zn_{20}

PNAS

Six closely related YbT_2Zn_{20} (T = Fe, Co, Ru, Rh, Os, Ir) heavy fermion compounds with large local moment degeneracy

M. S. Torikachvili*†, S. Jia*, E. D. Mun*, S. T. Hannahs‡, R. C. Black§, W. K. Neils§, Dinesh Martien§, S. L. Bud'ko*, and P. C. Canfield*¶

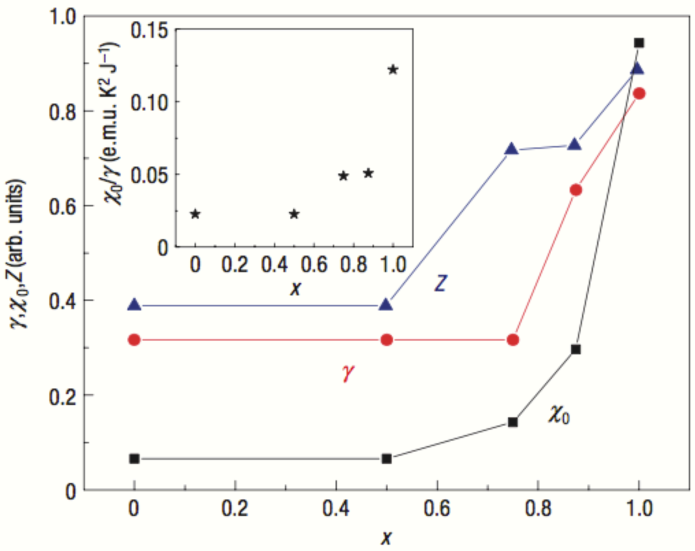


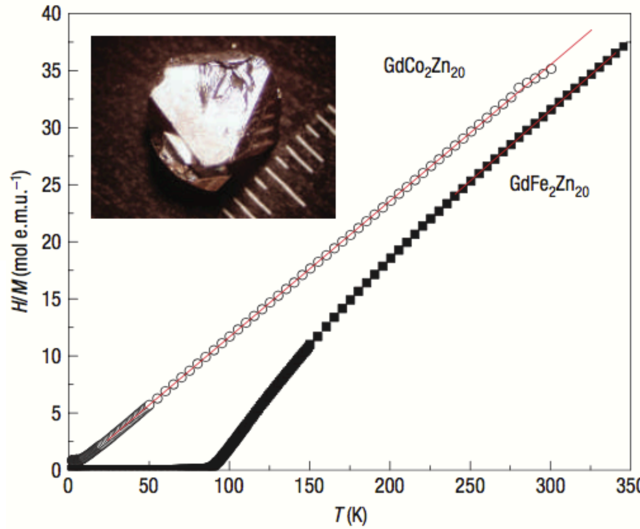
Cage Compounds RT_2Zn_{20}

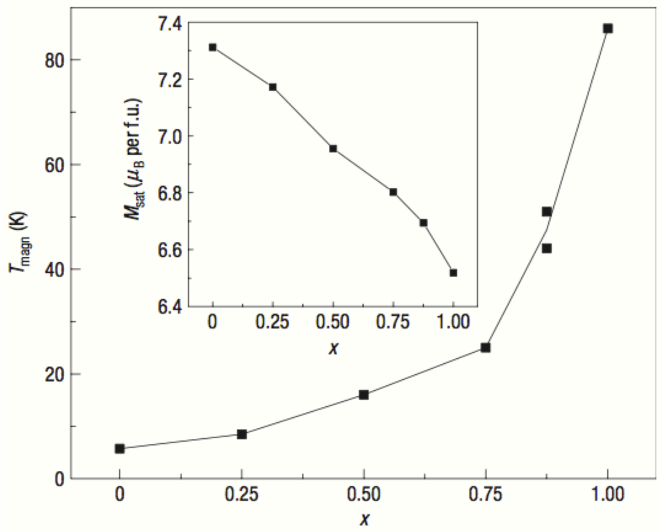
LETTERS

Nearly ferromagnetic Fermi-liquid behaviour in YFe_2Zn_{20} and high-temperature ferromagnetism of $GdFe_2Zn_{20}$

S. JIA[1], S. L. BUD'KO[1], G. D. SAMOLYUK[2] AND P. C. CANFIELD[1]*
[1]Ames Laboratory US DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
[2]Ames Laboratory US DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA
*e-mail: canfield@ameslab.gov







$GdCo_2Zn_{20}$: T_N ~ 6 K

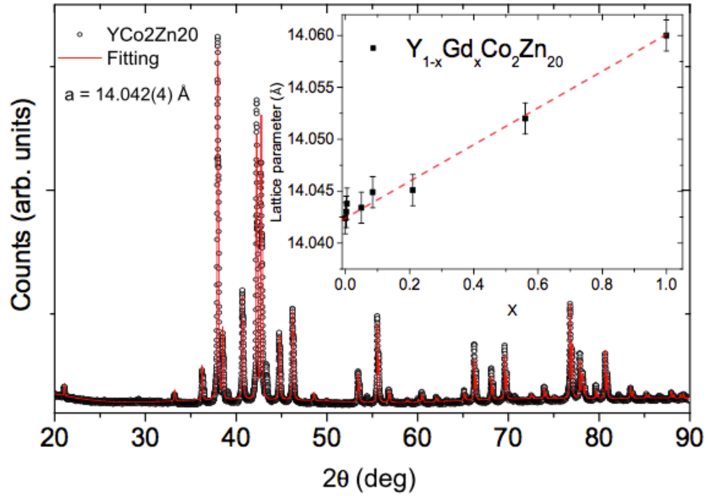
$GdFe_2Zn_{20}$: T_C ~ 86 K

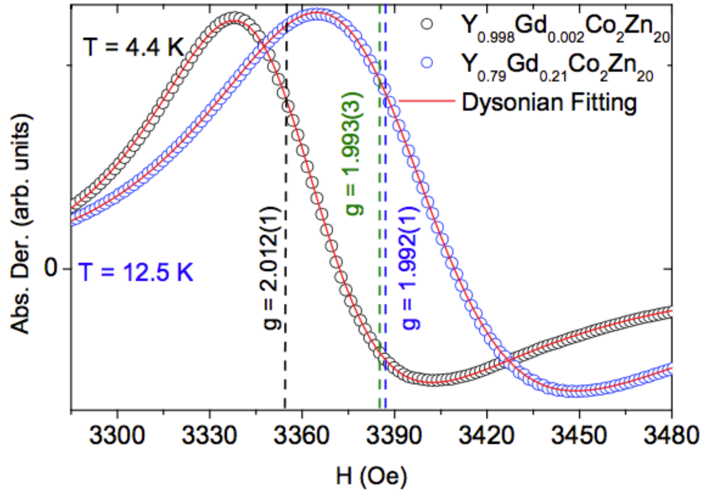
$Y_{1-x}Gd_xCo_2Zn_{20}$

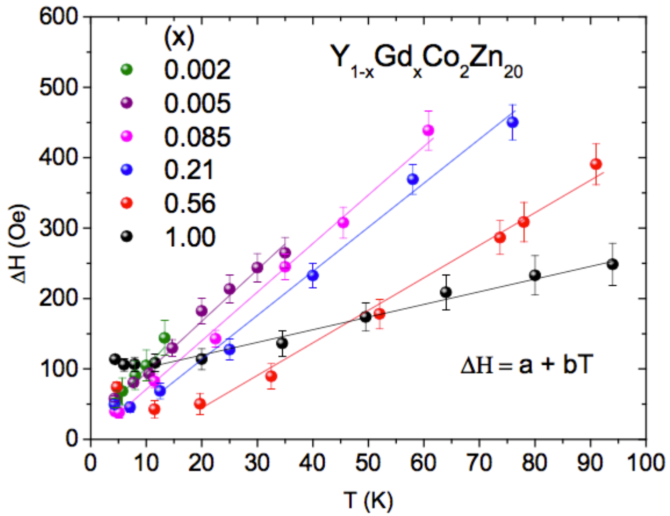
PHYSICAL REVIEW B **92**, 214414 (2015)

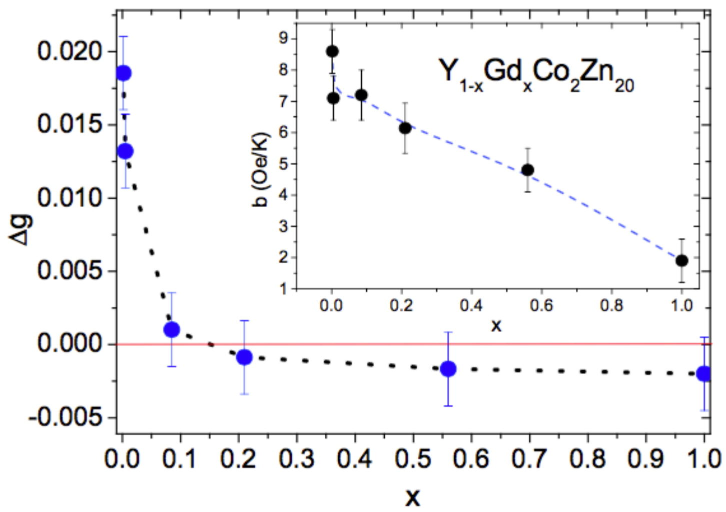
Multiband electronic characterization of the complex intermetallic cage system $Y_{1-x}Gd_xCo_2Zn_{20}$

M. Cabrera-Baez,[1] A. Naranjo-Uribe,[2] J. M. Osorio-Guillén,[2] C. Rettori,[1,3] and M. A. Avila[1,*]

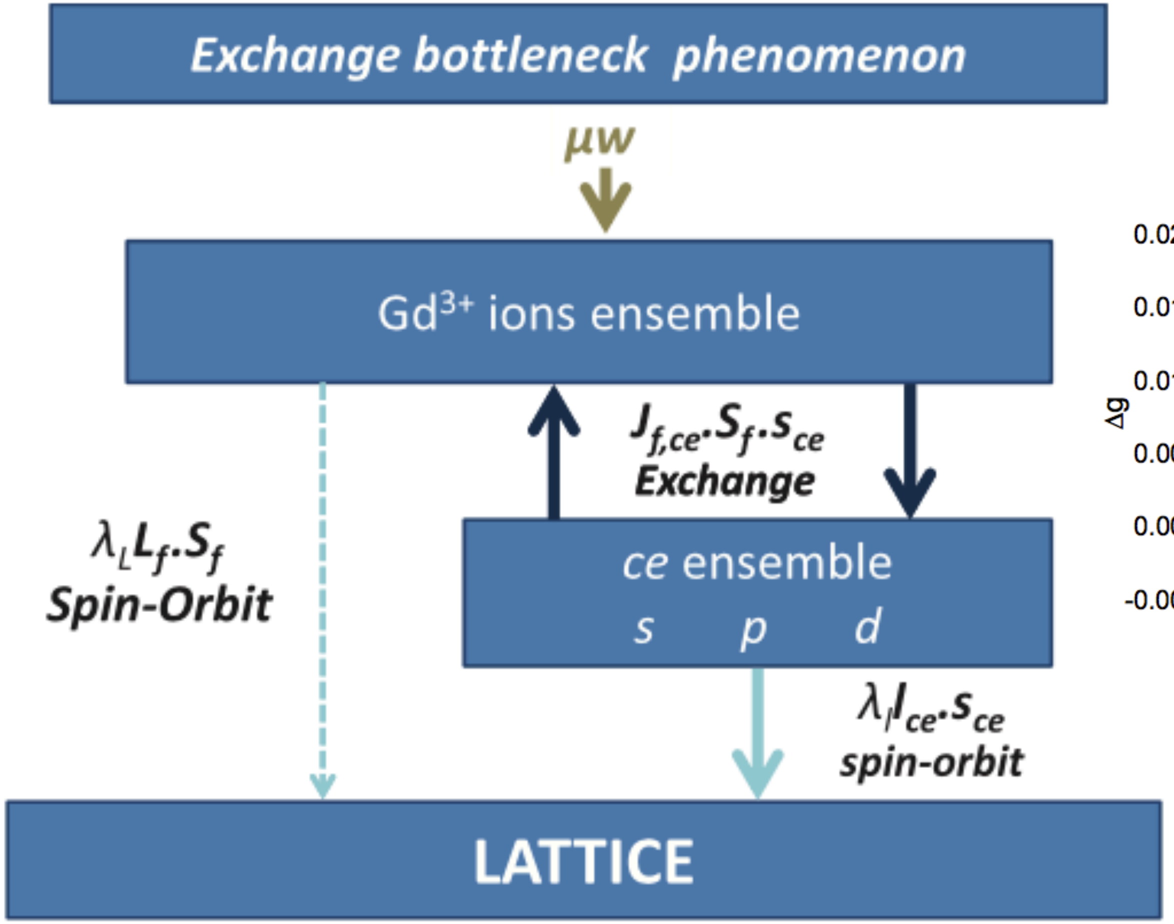


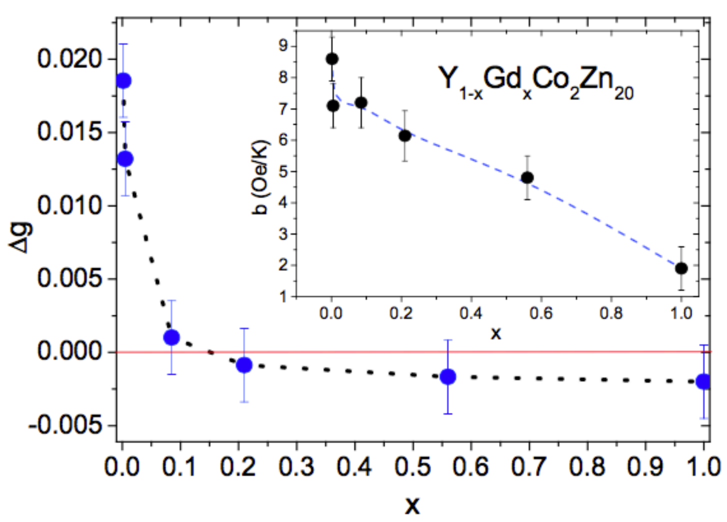






Exchange Bottleneck Effect





$Y_{1-x}Gd_xCo_2Zn_{20}$

Multiband analysis

$$\Delta g = \Delta g_{fs} + \Delta g_{fp} + \Delta g_{fd} = J_{fs}(0)\eta_{F_s} - J_{fp}(0)\eta_{F_p} + J_{fd}(0)\eta_{F_d} \quad (4)$$

and

$$b = \frac{\pi k_B}{g\mu_B}[F_s\Delta g_{fs}^2 + F_p\Delta g_{fp}^2 + F_d\Delta g_{fd}^2] = \frac{\pi k_B}{g\mu_B}[F_s\langle J_{fs}^2(q)\rangle_F \eta_{F_s}^2 + F_p J_{fp}^2(0)\eta_{F_p}^2 + F_d J_{fd}^2(0)\eta_{F_d}^2], \quad (5)$$

Extreme bottleneck regime

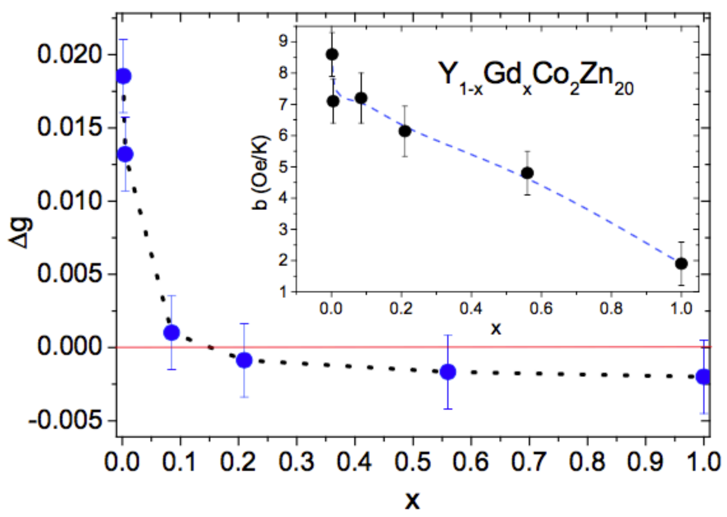
$$\Delta g = -0.002(2) = -J_{fp}(0)\eta_{F_p} + J_{fd}(0)\eta_{F_d}, \quad (6)$$

$$b = 1.9(6)\,\mathrm{Oe/K} = \frac{\pi k_B}{g\mu_B}[F_p J_{fp}^2(0)\eta_{F_p}^2 + F_d J_{fd}^2(0)\eta_{F_d}^2]. \quad (7)$$

Unbottleneck regime

$$\Delta g = 0.019(2) = J_{fs}(0)\eta_{F_s} - 0.002(2), \quad (8)$$

$$b = 8.6(6)\,\mathrm{Oe/K} = \frac{\pi k_B}{g\mu_B}[F_s\langle J_{fs}^2(q)\rangle_F \eta_{F_s}^2] + 1.9(6). \quad (9)$$



$Y_{1-x}Gd_xCo_2Zn_{20}$

PHYSICAL REVIEW B **92**, 214414 (2015)

Multiband electronic characterization of the complex intermetallic cage system $Y_{1-x}Gd_xCo_2Zn_{20}$

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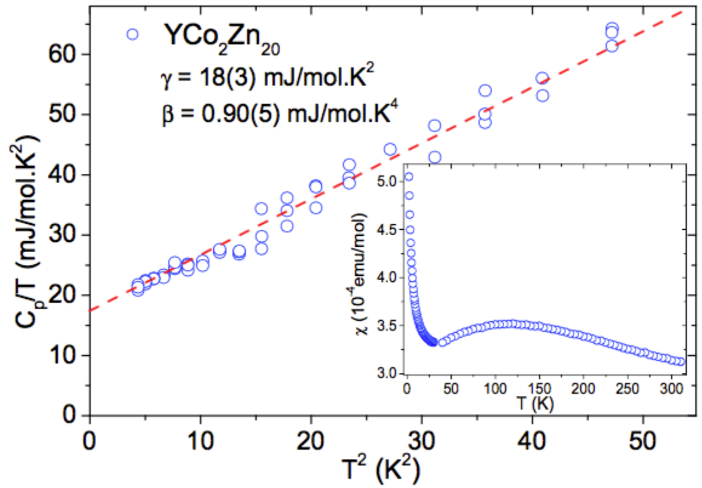

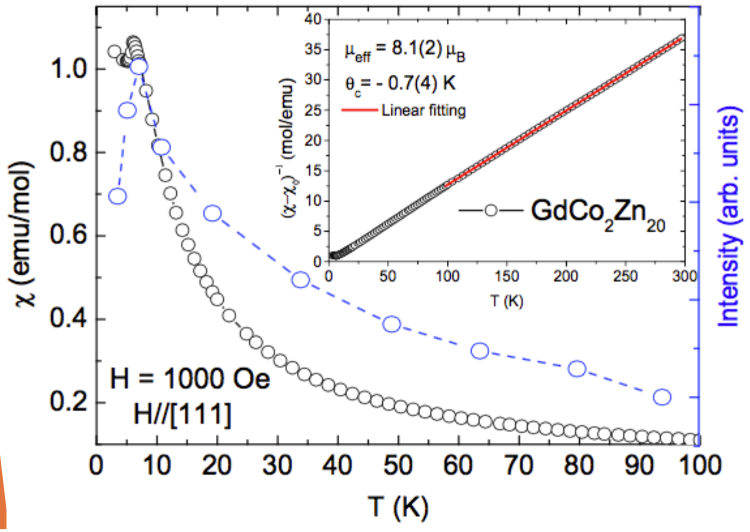

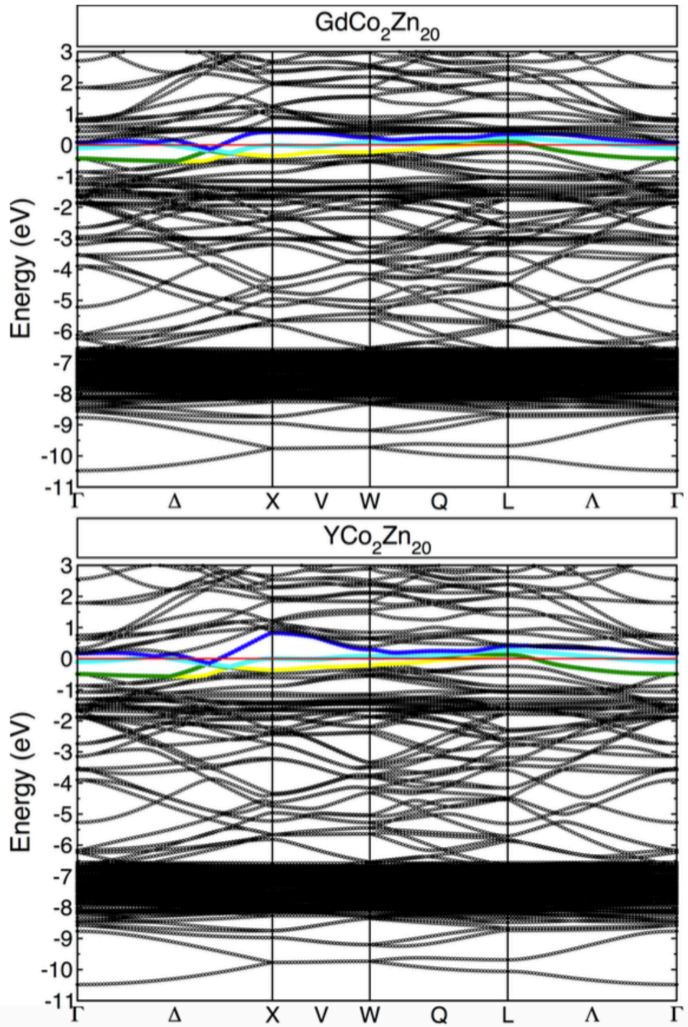

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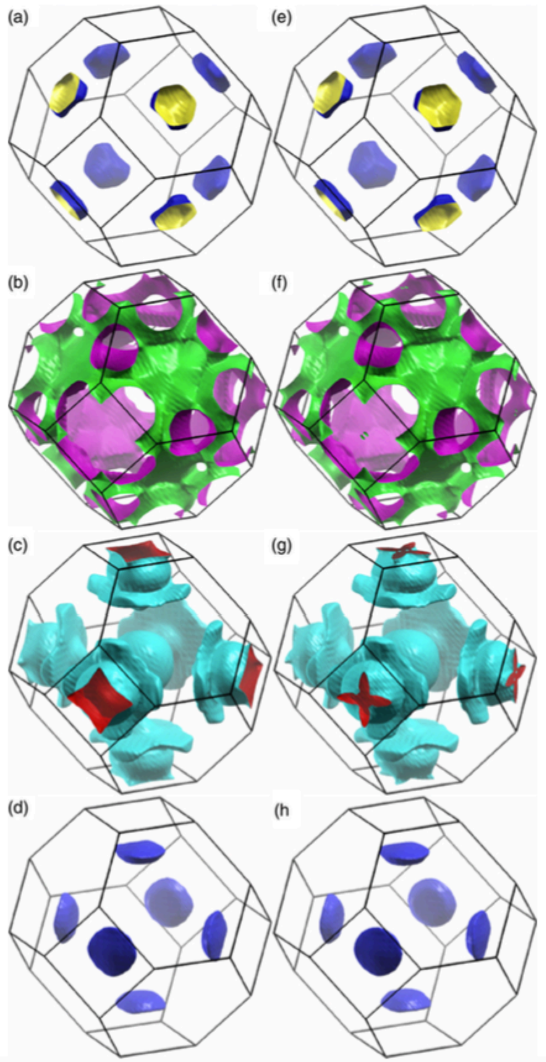

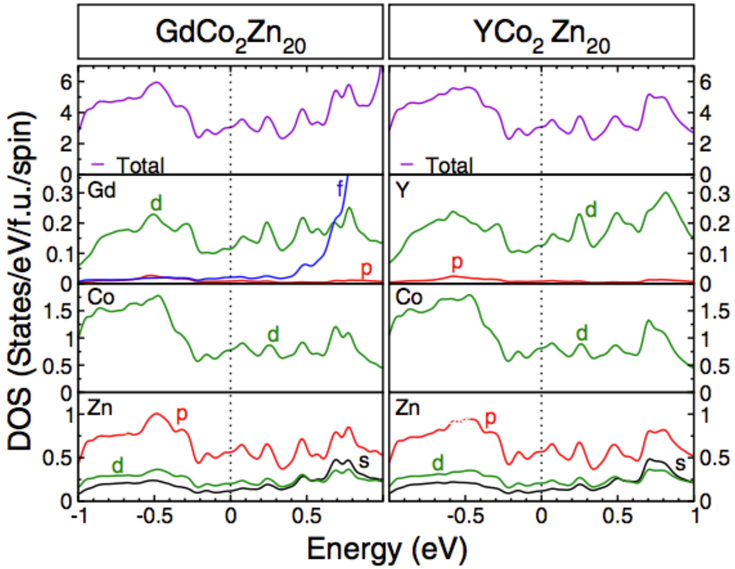

$$J_{fd}(0) = 10(5) \text{ meV and } J_{fp}(0) = 22(6) \text{ meV.}$$

$$J_{fs}(0) = 167(7) \text{ meV} \quad \langle J^2_{fs}(q)\rangle^{1/2}_F = 18(5) \text{ meV}$$

$J_{fs}(0)$ **dominant** interaction

$Y_{1-x}Gd_xCo_2Zn_{20}$

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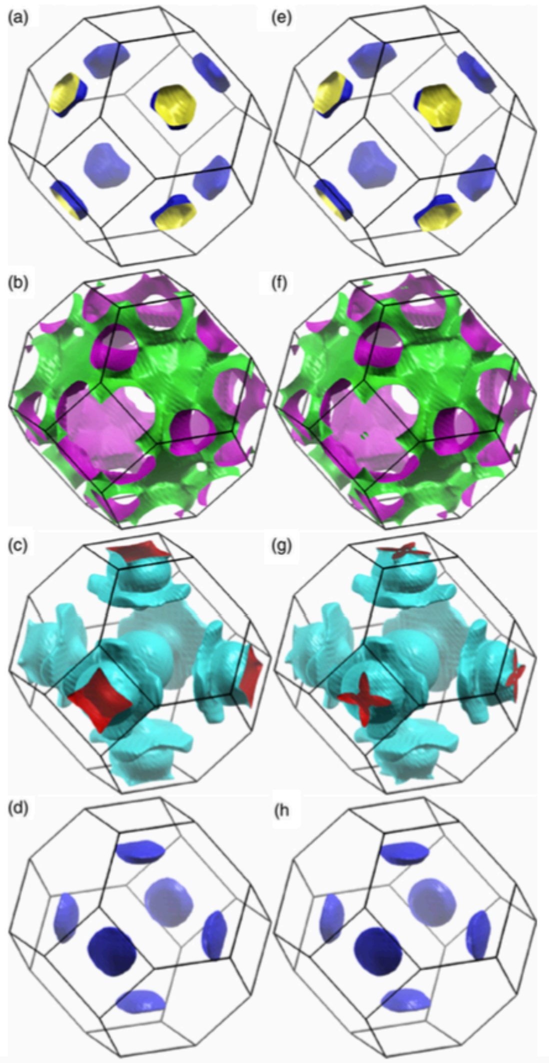
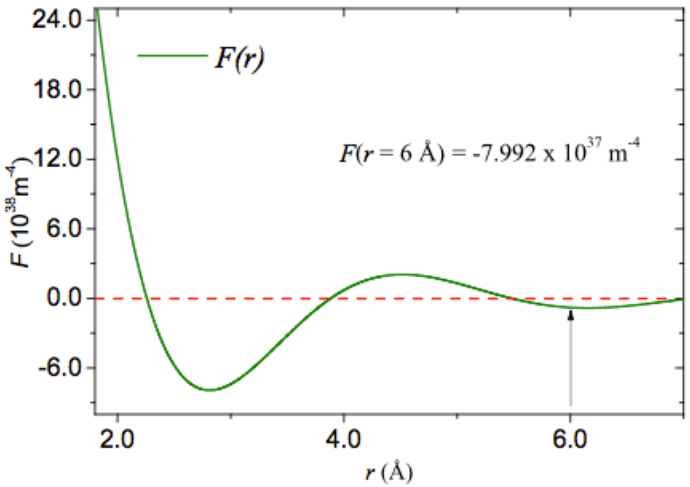




$$J_{eff} \approx \frac{9\pi(J_{fs}(0))^2\nu^2F(r)}{64E_F(2K_F)^4}$$

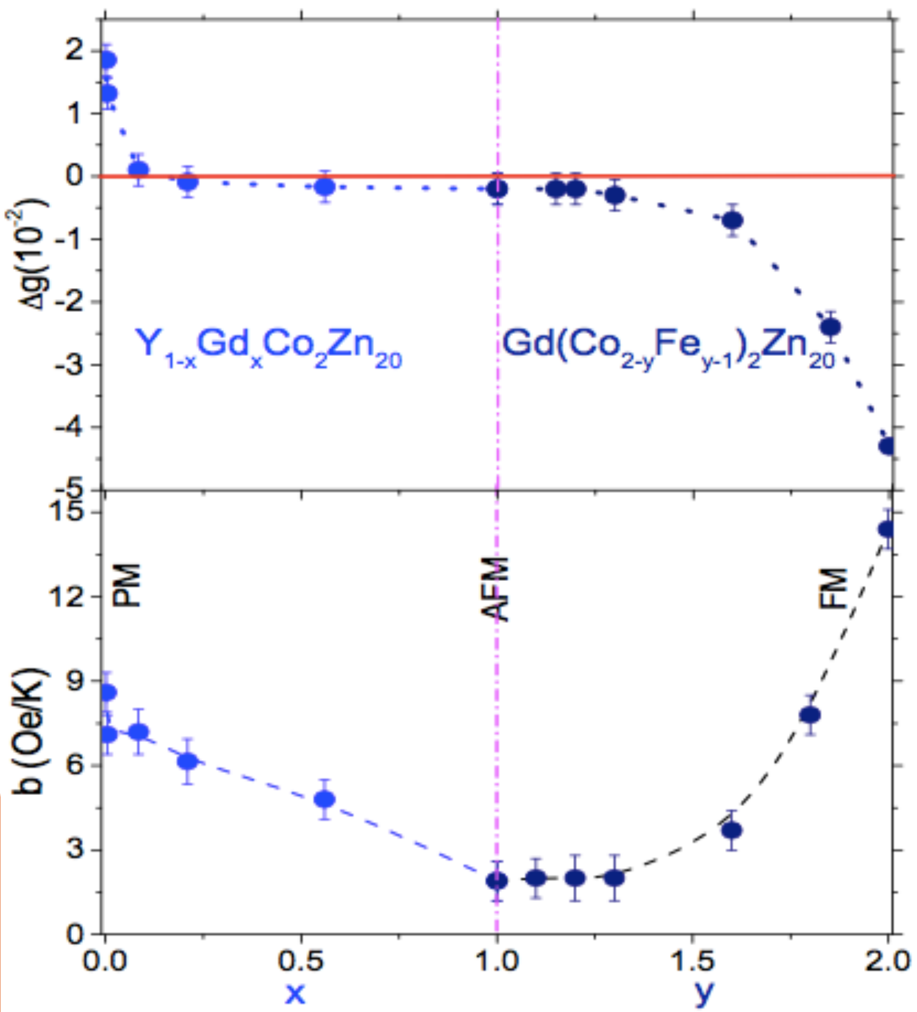
$$J^*_{eff} = dG \times J_{eff} = -0.040(4)\ \text{meV}.$$

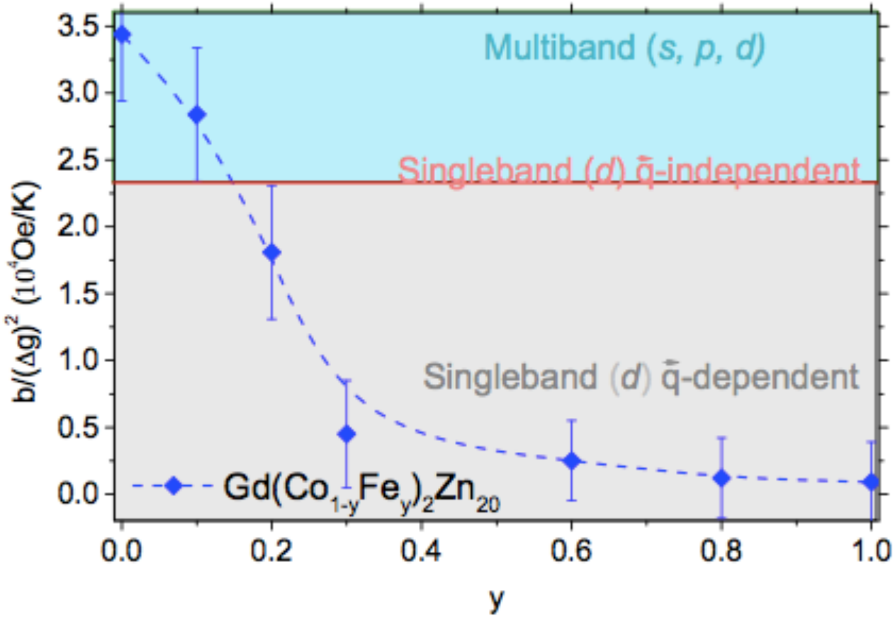
$$\theta_C = \frac{2ZJ^*_{eff}}{3K_B}$$ = -1.2(2) K [Exp: -0.7(4) K]

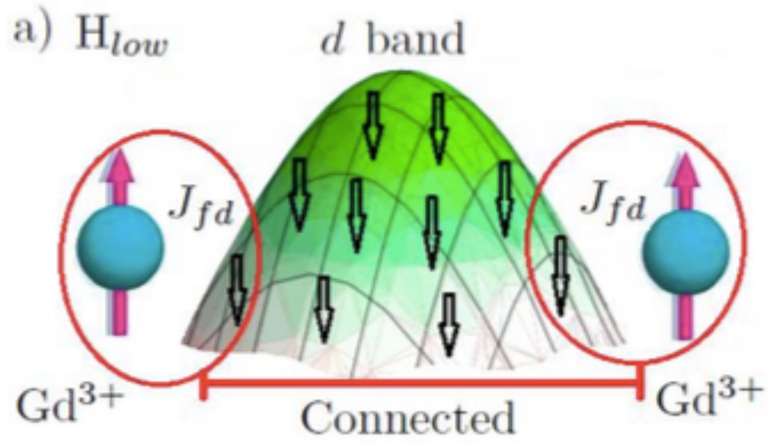
Model RKKY system!

First connection between micro and macro

Current Work – $Gd(Co_{1-y}Fe_y)_2Zn_{20}$



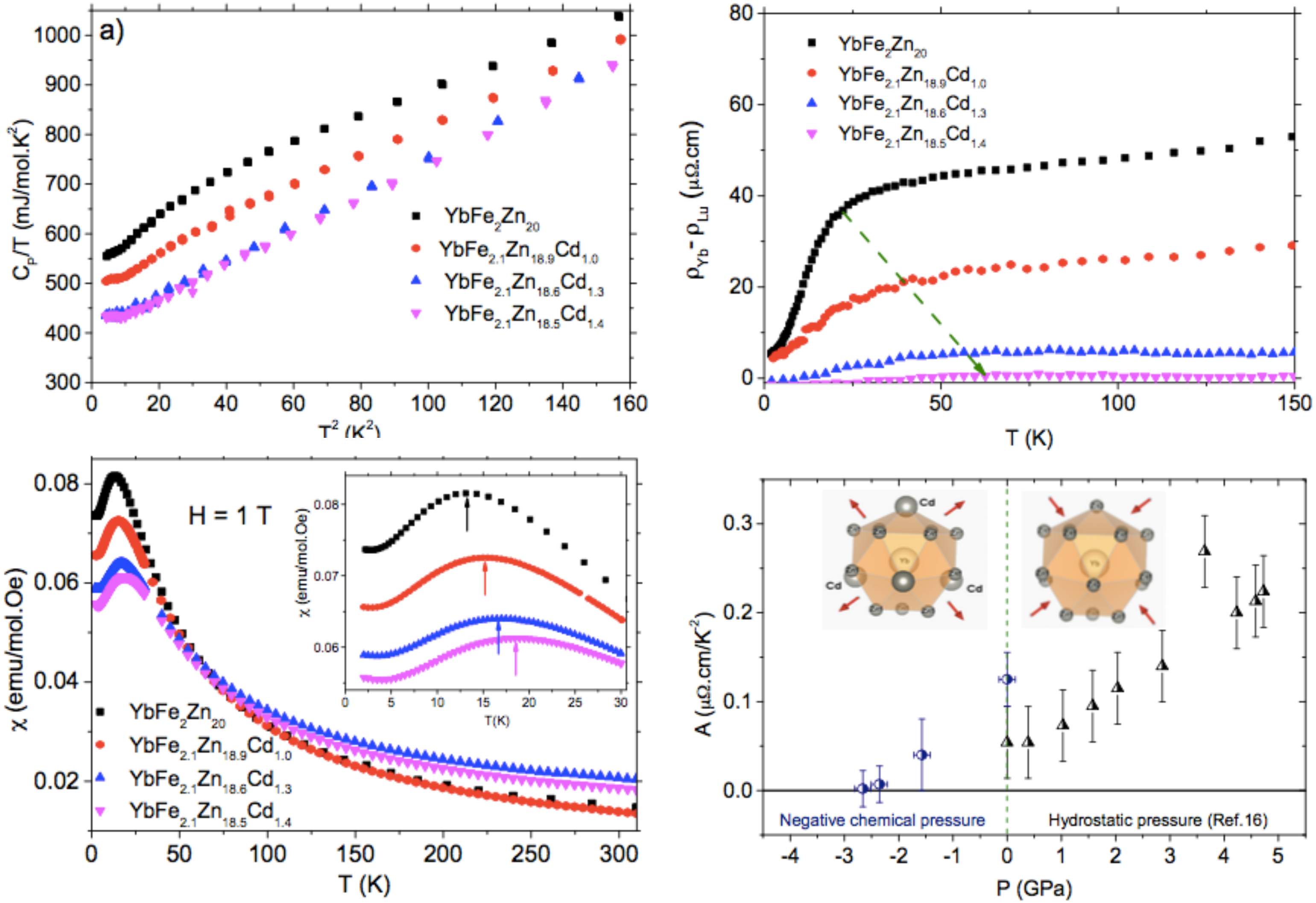




Current Work – $YbFe_2Zn_{20-x}Cd_x$

Tuning the electronic hybridization in the heavy fermion cage compound $YbFe_2Zn_{20}$ with Cd-doping

M. Cabrera-Baez, R. A. Ribeiro and M. A. Avila



Summary

- Thermoelectrics
  - Noble motivation to seek out next generation of energy materials that may also feature novel, exciting physics

- $FeGa_3$
  - Simple diamagnetic semiconducting material in which surprisingly complex physics emerge with Ge doping

- RT_2Zn_{20}
  - Complex cage compounds in which surprisingly simple and tractable physics are revealed in the non-hybridizing compounds.

Both cases successful due to **synergetic efforts** between experiment and DFT simulations

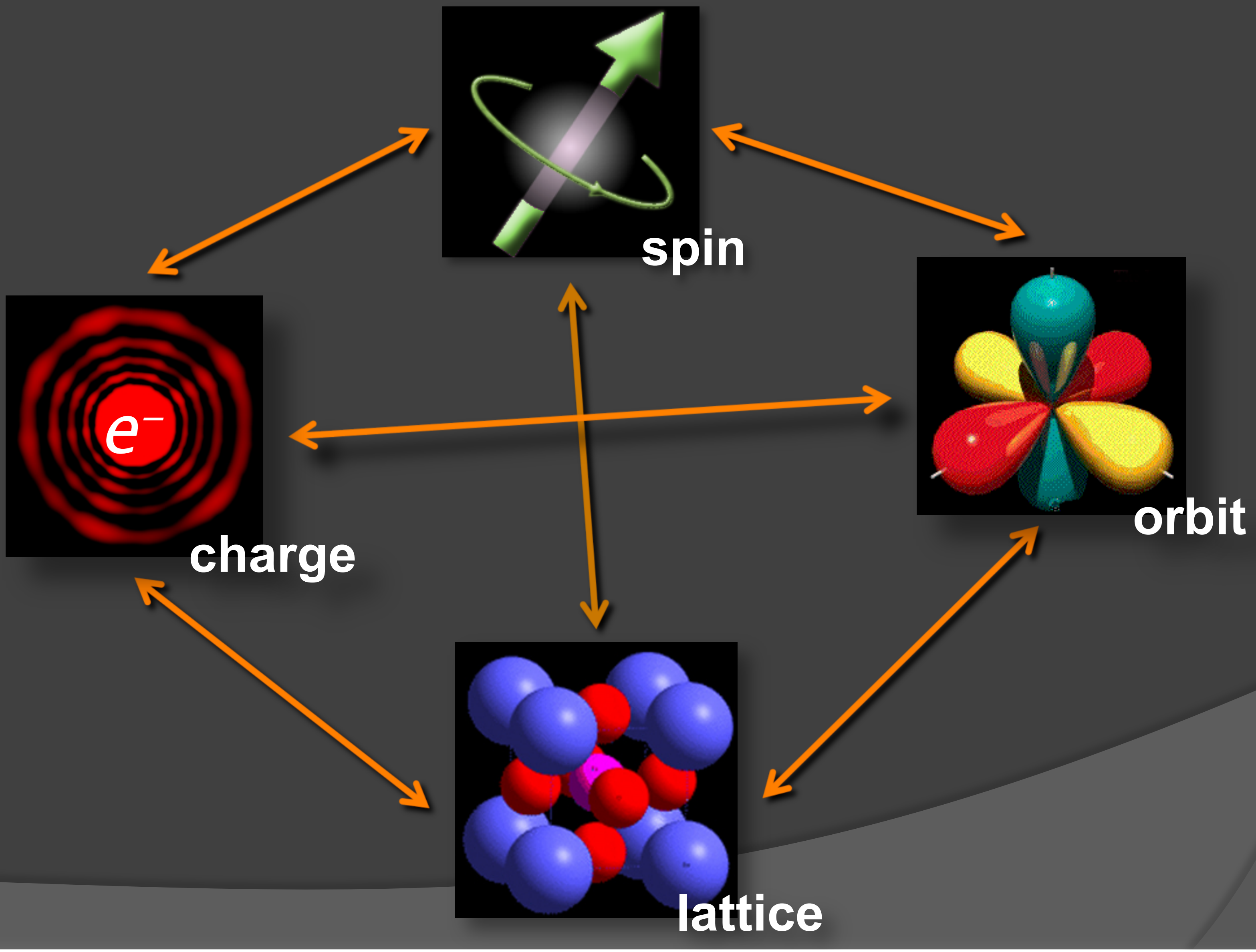
Marcos A. Avila
Raquel A. Ribeiro
Letície M. Ferreira
Carlos Rettori

GMQ

GRUPO DE MATERIAIS QUÂNTICOS

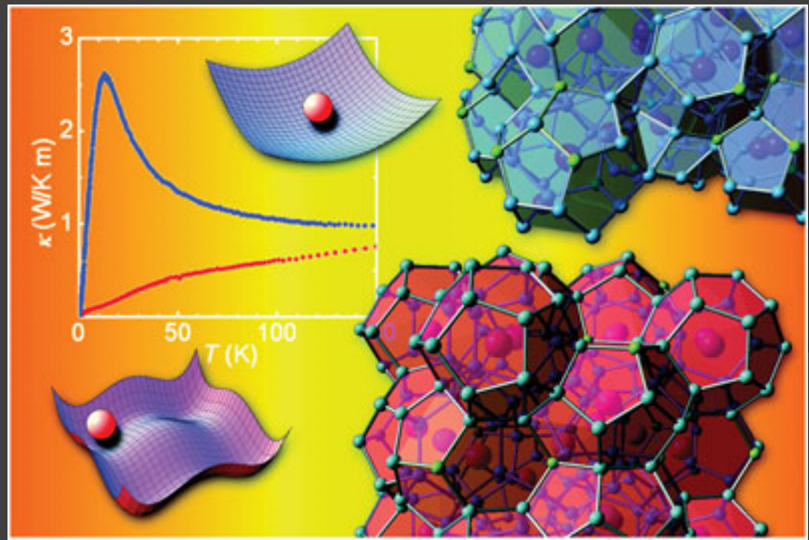
Universidade Federal do ABC

Area: Condensed Matter Physics

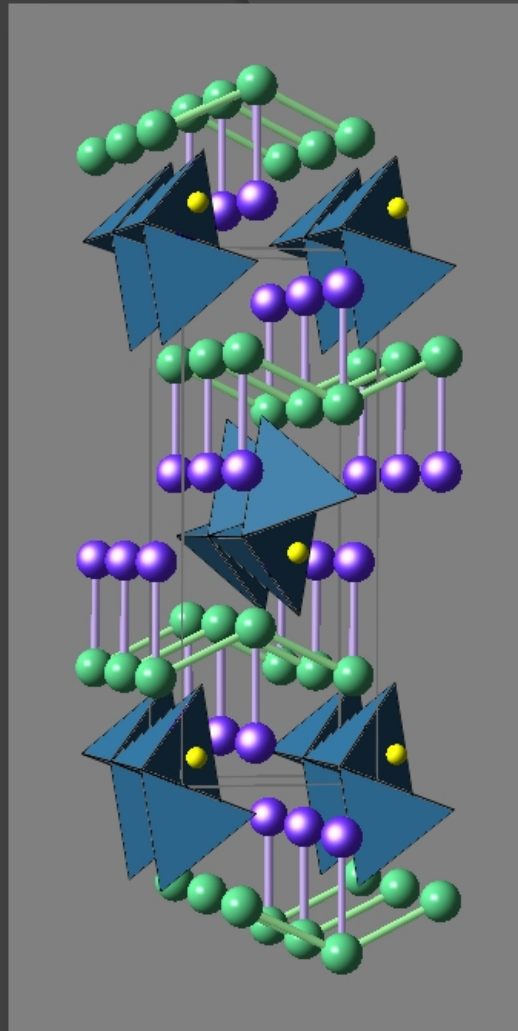


Research Focus

- Design, development and discovery of novel materials with academic or functional interest, particularly those that exhibit:
  - Strongly Correlated Electrons;
  - Termoelectricity;
  - Magnetism;
  - Superconductivity;
  - Quantum Criticality



Methodologies



- Combine elements into compounds
  - MgB_2 , $Yb_{14}MnSb_{11}$, $YBa_2Cu_3O_{7-x}$ ...
- Determine crystalline structures
  - Cubic, tetragonal, hexagonal ...
- Characterize physical properties
- Modify/optimize desired properties
- Use as model systems to:
  - Advance understanding of physical problems;
  - Seek solutions for current application demands

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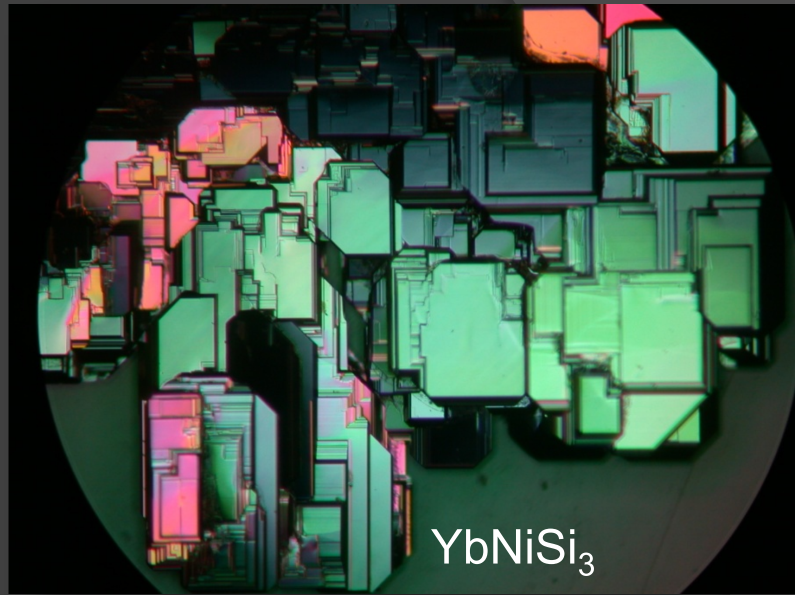
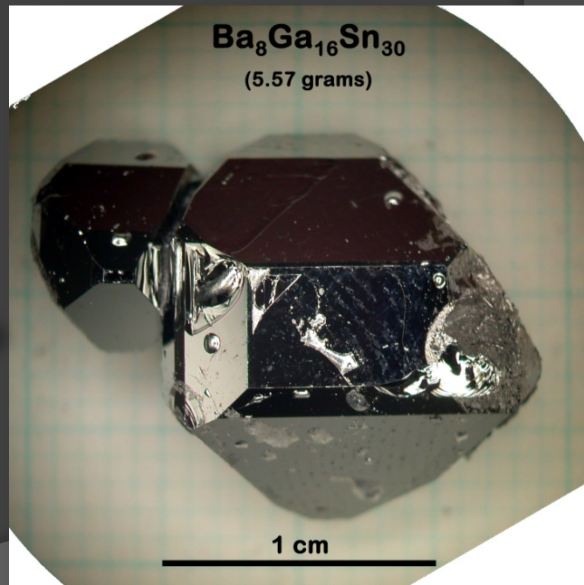
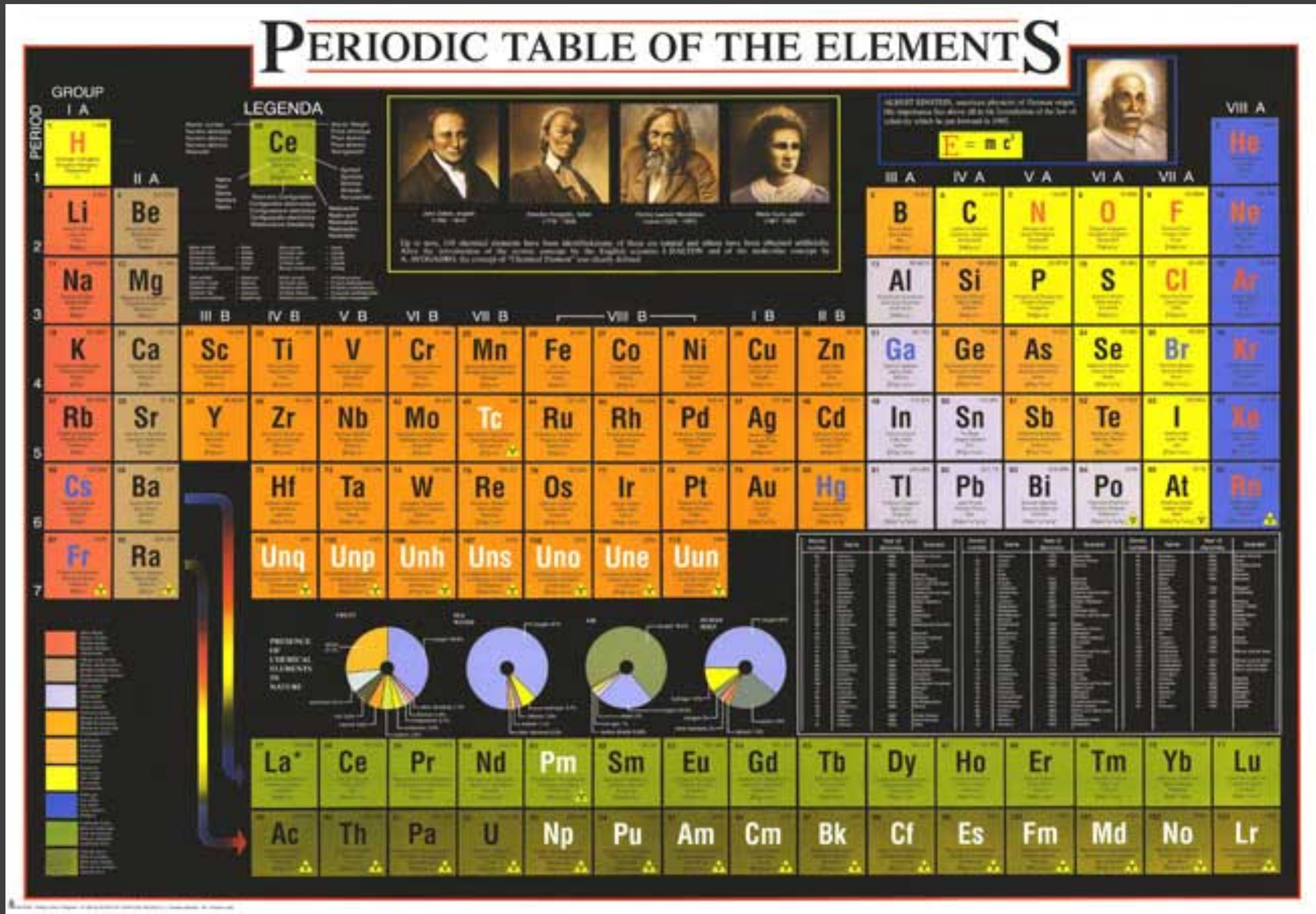
Recent Examples

- Binaries
  - MgB_2, YbB_2, $FeGa_3$, YIn_3
- Ternaries
  - RT_2X_2, R_2TX_6, $YbNiX_3$
  - RPd_5Al_2, AFe_2As_2
  - RT_4X_{12}, $Yb_{14}TSb_{11}$, $A_8M_{16}X_{30}$
- Quaternaries
  - $RBa_2Cu_3O_{7-x}$, RNi_2B_2C





Playground


PERIODIC TABLE OF THE ELEMENTS
GROUP
I A
PERIOD
LEGENDA
II A
III A IV A V A VI A VII A
VIII A
III B IV B V B VI B VII B VIII B I B II B
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Unq Unp Unh Uns Uno Une Uun
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Prospection Status

Systems	Stage
Pure Elements	95%
Binary Compounds	75%
Ternary Compounds	25%
Quaternary Compounds	5%

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