The 17 position knob:

Tuning interactions with rare earths

Paul C. Canfield

Distinguished Professor of Physics

Senior Physicist, Ames Lab

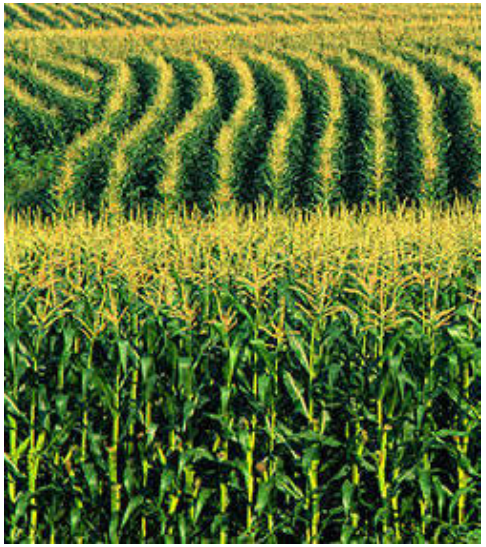
Iowa State University

Boulder 2008 Summer School

Iowa State University 150 Years of Land-Grant Education

~ 25,000 Students

Known for Ag. (not Silver), Vet., and, in our circles, Physics and Chemistry associated with Ames Lab.



Ames Laboratory

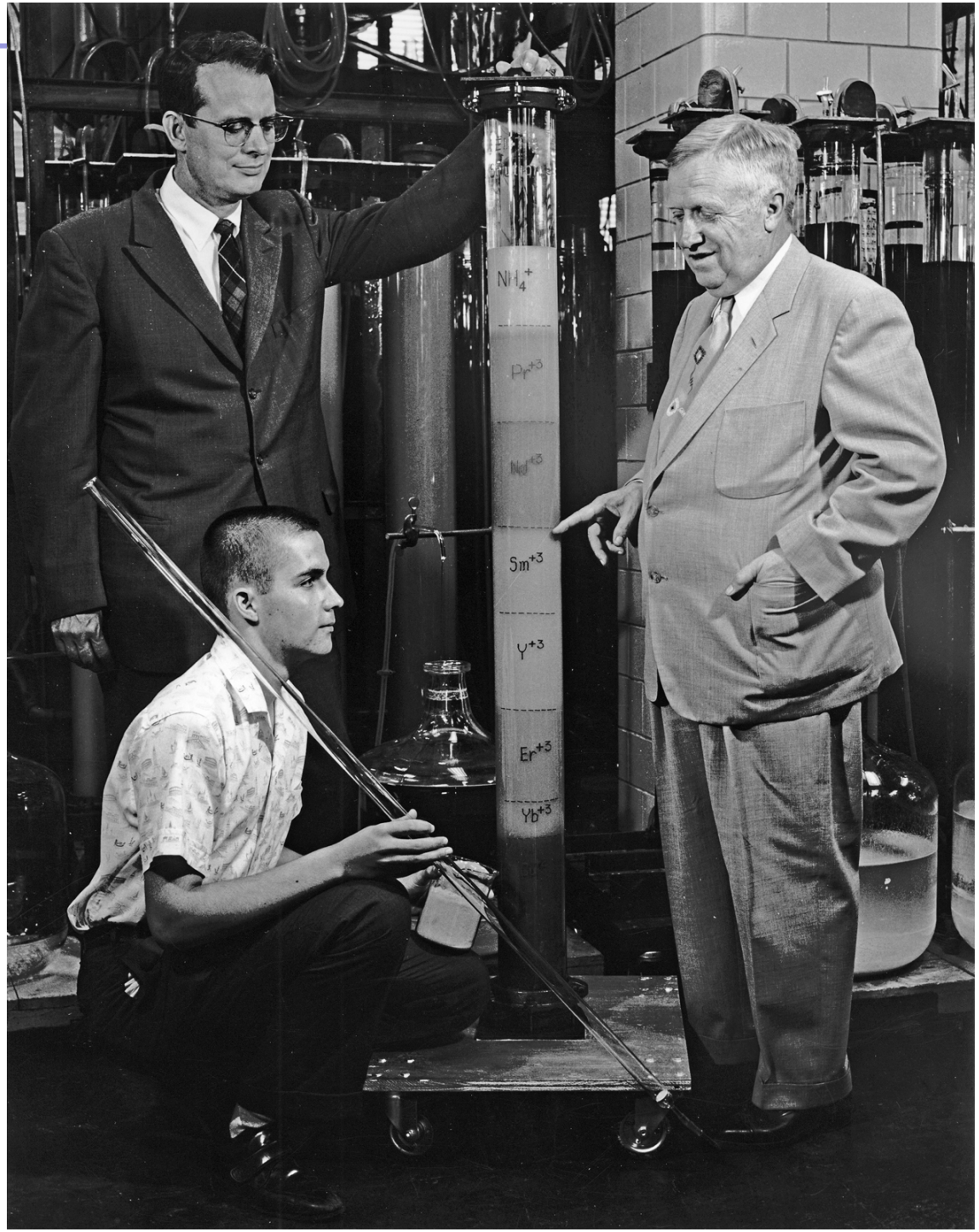
Frank Spedding

Ames Lab was the starting point for the materials used in the Manhattan project. Soon after WWII it became a basic science lab.

DOE OFFICE OF SCIENCE LABORATORIES

Frank Spedding (right) examines a demonstration column showing the separation of the rare earths with senior chemist Jack Powell (standing) and summer student trainee Tom Erskine. This photo was featured in a 1963 Sunday edition of the *Des Moines Register*

Ames Lab still produces (and sells) the world's highest purity rare earth elements. Please contact Larry Jones or Tom Lograsso about getting quotes or information.



Ames Laboratory

Ames Laboratory facilities are located on Pammel Drive on the north edge of the Iowa State University campus.

For 60 years Ames Laboratory has been a leader in the physics, chemistry and metallurgy of novel materials.

Mid-sized DOE Laboratory with ~ 400 employees

Now:

Applied Mathematics and Computational Sciences

Chemical and Biological Sciences

Condensed Matter Physics

Environmental and Protection Sciences

Granular and Multiphase Systems

Materials Chemistry

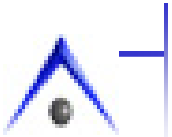
Materials and Engineering Physics

Non-Destructive Evaluation

Also:

Biorenewable Resources Consortium

Materials Preparation Center



Ames Laboratory

Novel Materials and Ground States

Introduction | Members | Facilities | Publications | Photo Gallery | Links

You are here: Ames Laboratory > Condensed Matter Physics > Novel Materials

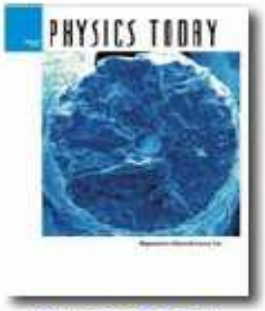
CANFIELD'S RESEARCH GROUP

Welcome to our web page, where you may learn about who we are and what we do as part of the Condensed Matter Physics Group of the Physics and Astronomy Department at Iowa State University and Ames Laboratory (a U. S. Department of Energy (DOE) facility). Our group of faculty, staff, post-docs, graduate and undergraduate students is mostly dedicated to the design, discovery, growth and characterization of novel electronic and magnetic compounds - often in single crystal form - and the study of their interesting physical properties.

Here are four of our general review articles:

Physics Today - October 1998
"New Magnetic Superconductors: A Toy Box for Solid-State Physicists"

Physics World - January 2002
"Magnesium Diboride: one year on"



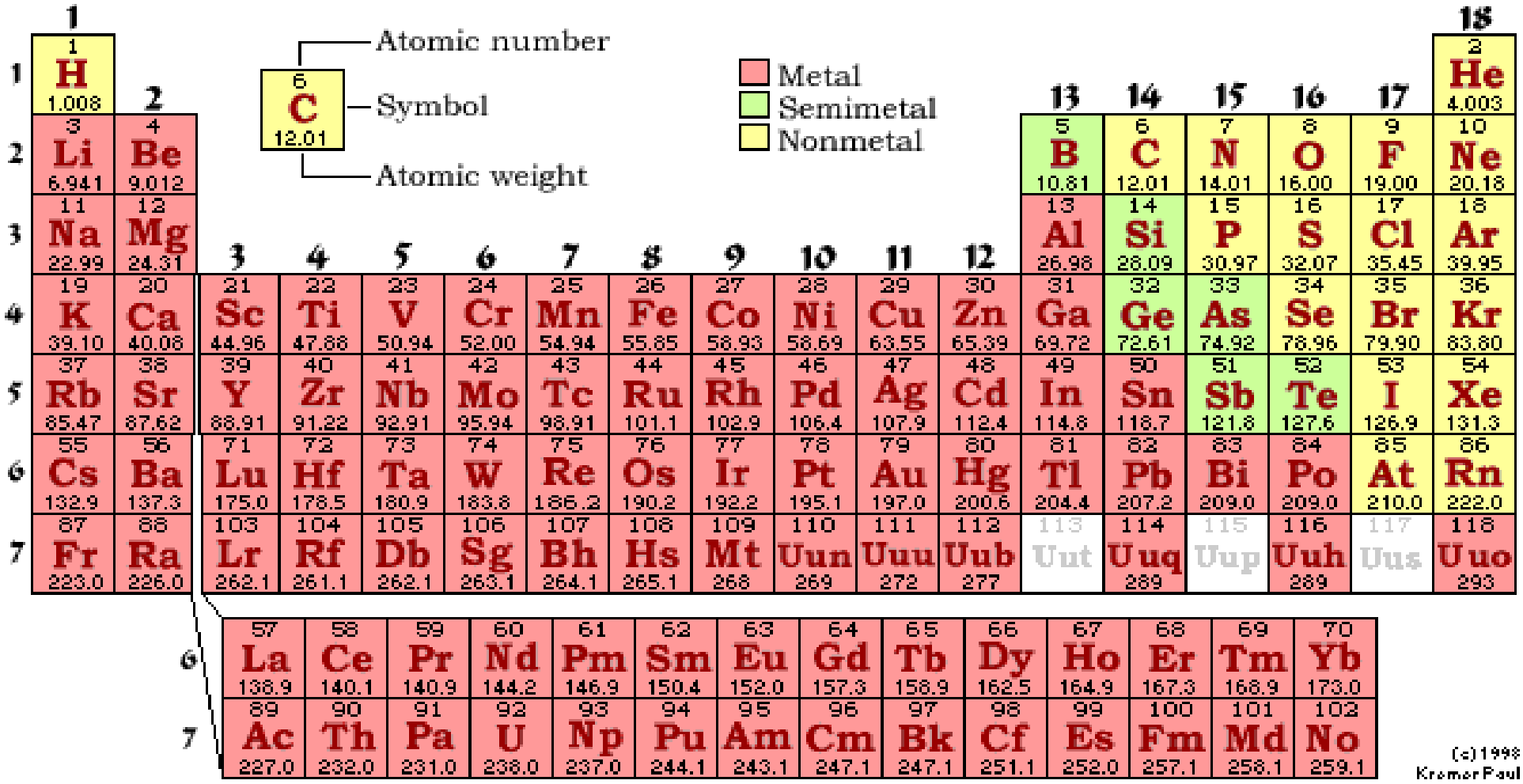
Physics Today - March 2003
"Magnesium Diboride: Better Late than Never"

Scientific American - April 2005
"Low Temperature Superconductivity Is Warming Up"

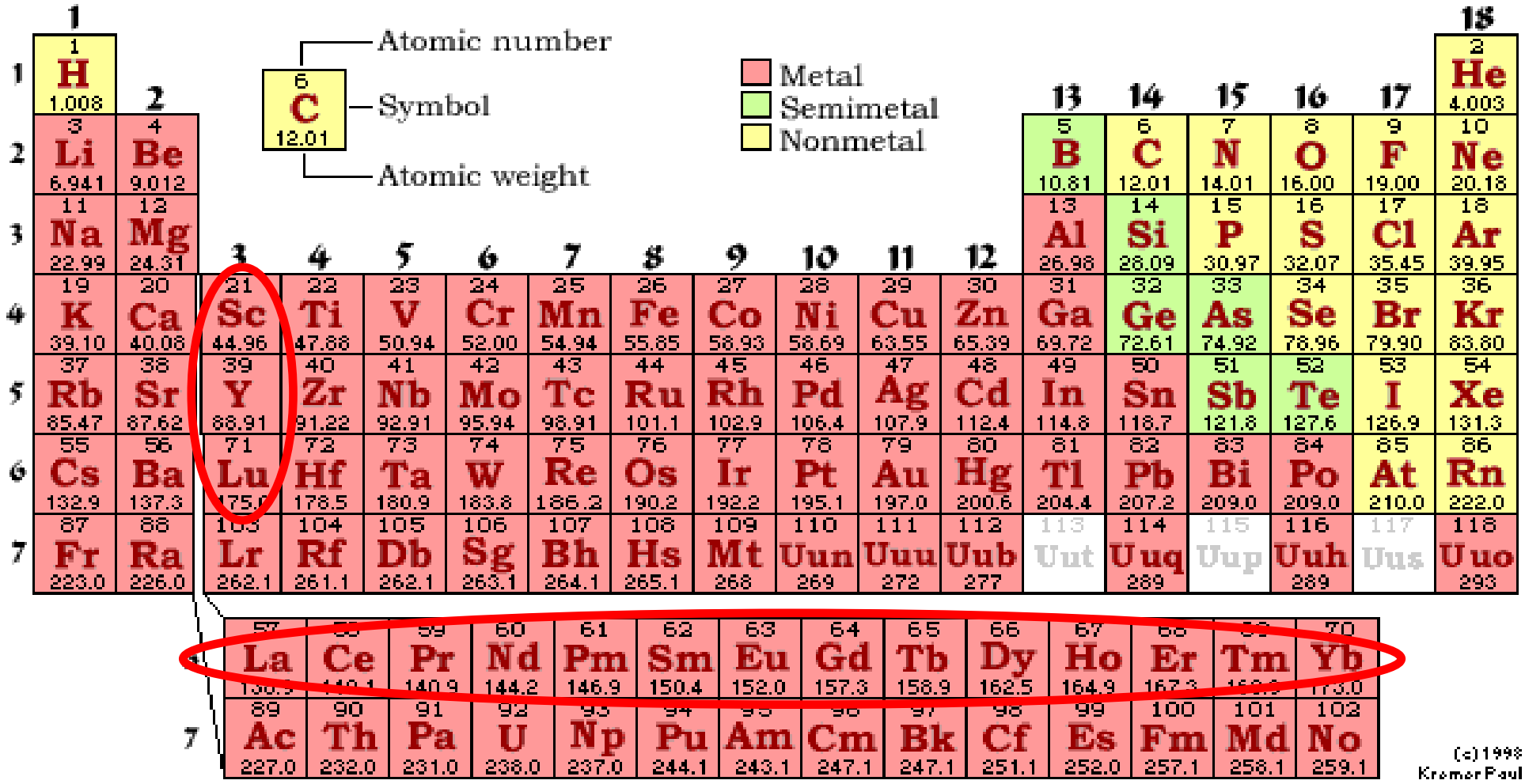
If the material I cover is of interest to you explore our home page. We have review articles, lists of activities, papers, people, and even some recipes.

http://cmpweb.ameslab.gov/personnel/canfield/

The periodic table is a palette, it is a well stocked pantry, it is the menu to choose your meal from, it is the ultimate puzzle box, it is the end all of DIY projects. It is the basis set that we have to work with.



The solid state physicist sees a powerful tuning mechanism.

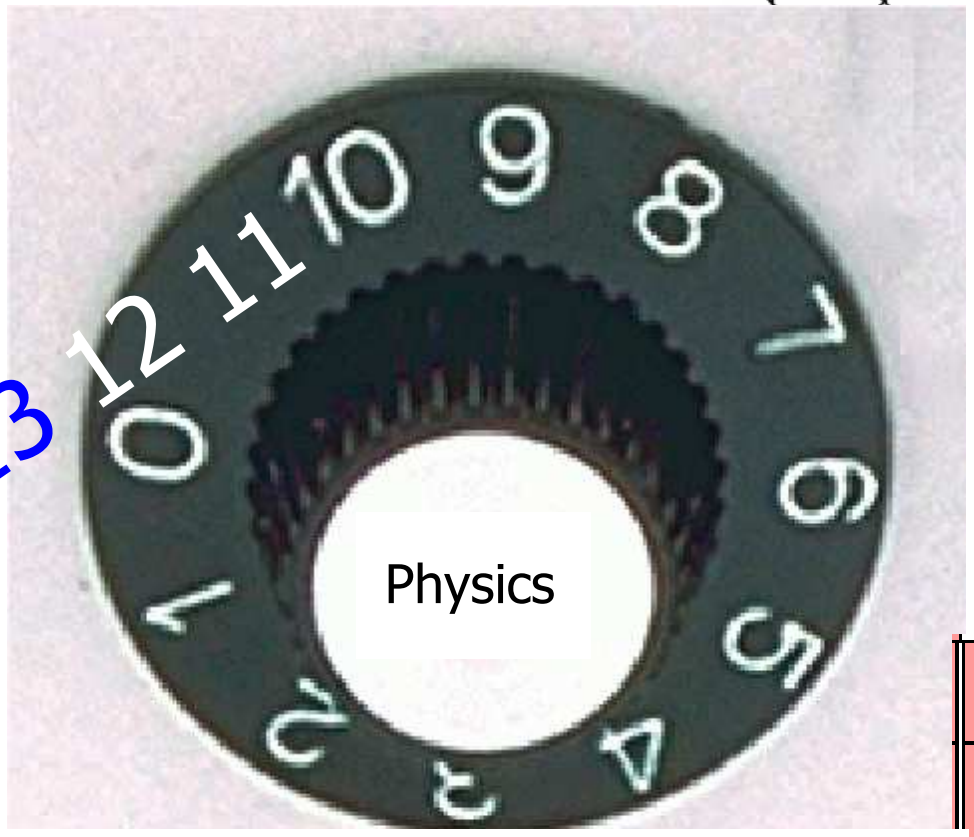


The rare earth elements can be chemically similar, but have vastly different magnetic properties. In RXY compounds you can dial in magnetism and tune other physical properties.

So how does a physicist look at (and use) the rare earth elements to get at "the physics" of novel materials?

The physicist sees a 17 position knob

For tuning magnetic, electronic and structural properties.



21	39	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
44.96	88.91	138.9	140.1	140.9	144.2	146.9	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0

By using the rare earths, the physicist can tune the:

Size of the unit cell,

Size of the local moment and degree of coupling,

Size and direction of anisotropy,

Amount of entropy that can be removed at low temperatures,

Band filling,

Degree of hybridiztion.

In terms of temperature and energy scales (another obsession of the physicist), the rare earths can be used to tune:

The magnetic ordering temperature T_C or T_N

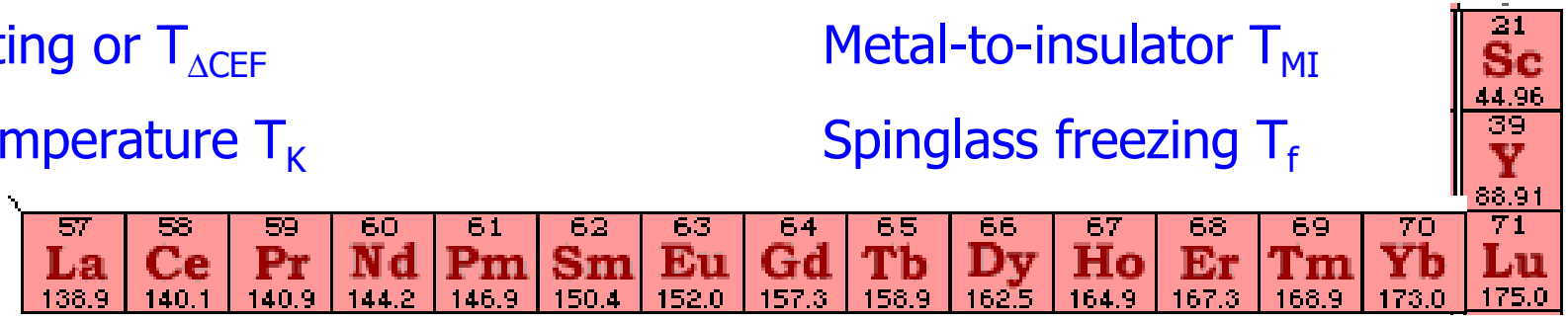
The CEF splitting or $T_{\Delta CEF}$

The Kondo temperature T_K

Superconducting T_C

Metal-to-insulator T_{MI}

Spinglass freezing T_f



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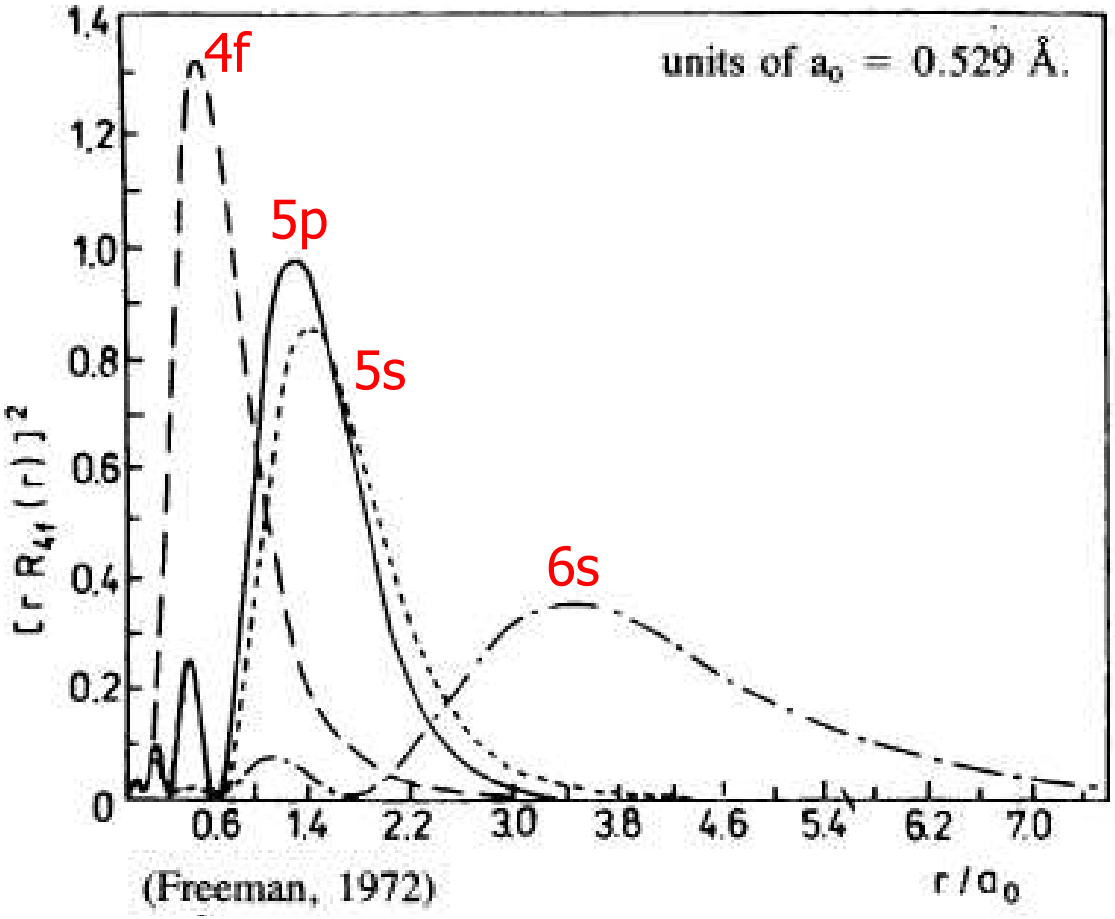
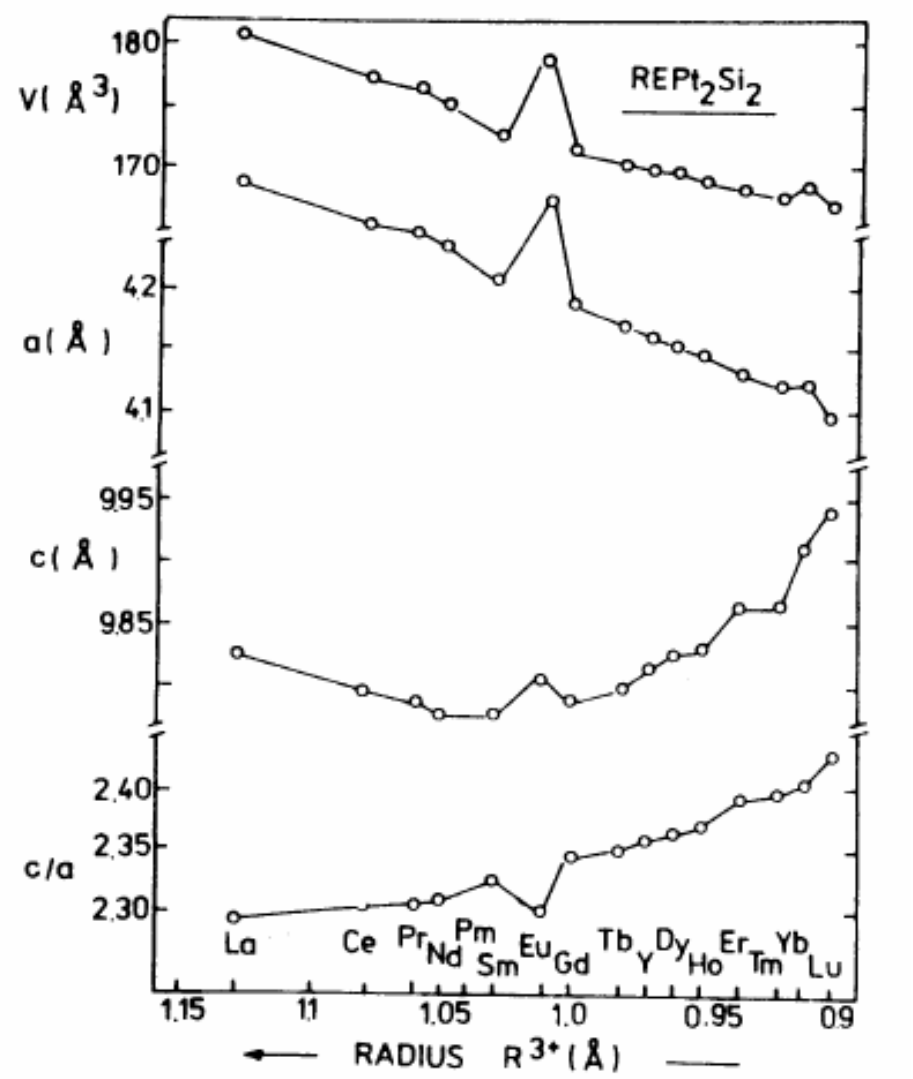
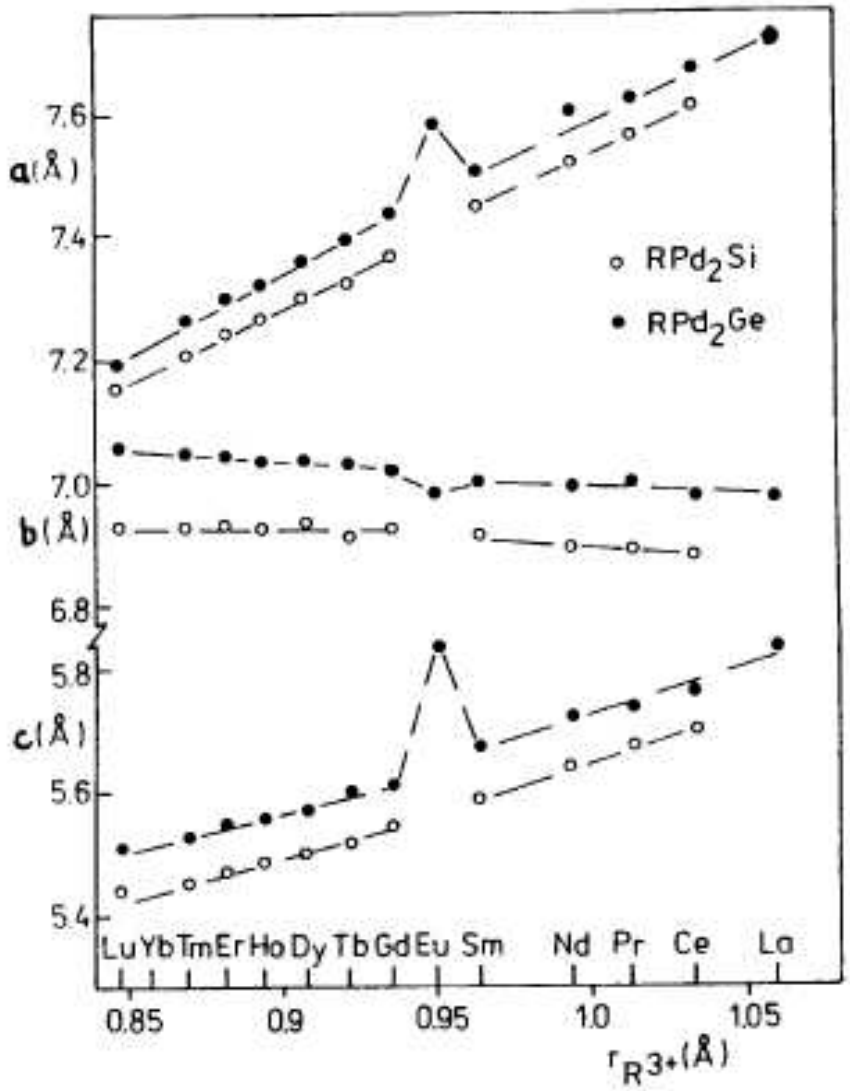
If you can make one member of a RXY series you (usually) can make several. This is due to the fact that the 4f-orbits are shielded by core levels and do not take part in bonding.

There is a structural effect of such substitutions though, ***the lanthanide contraction***.



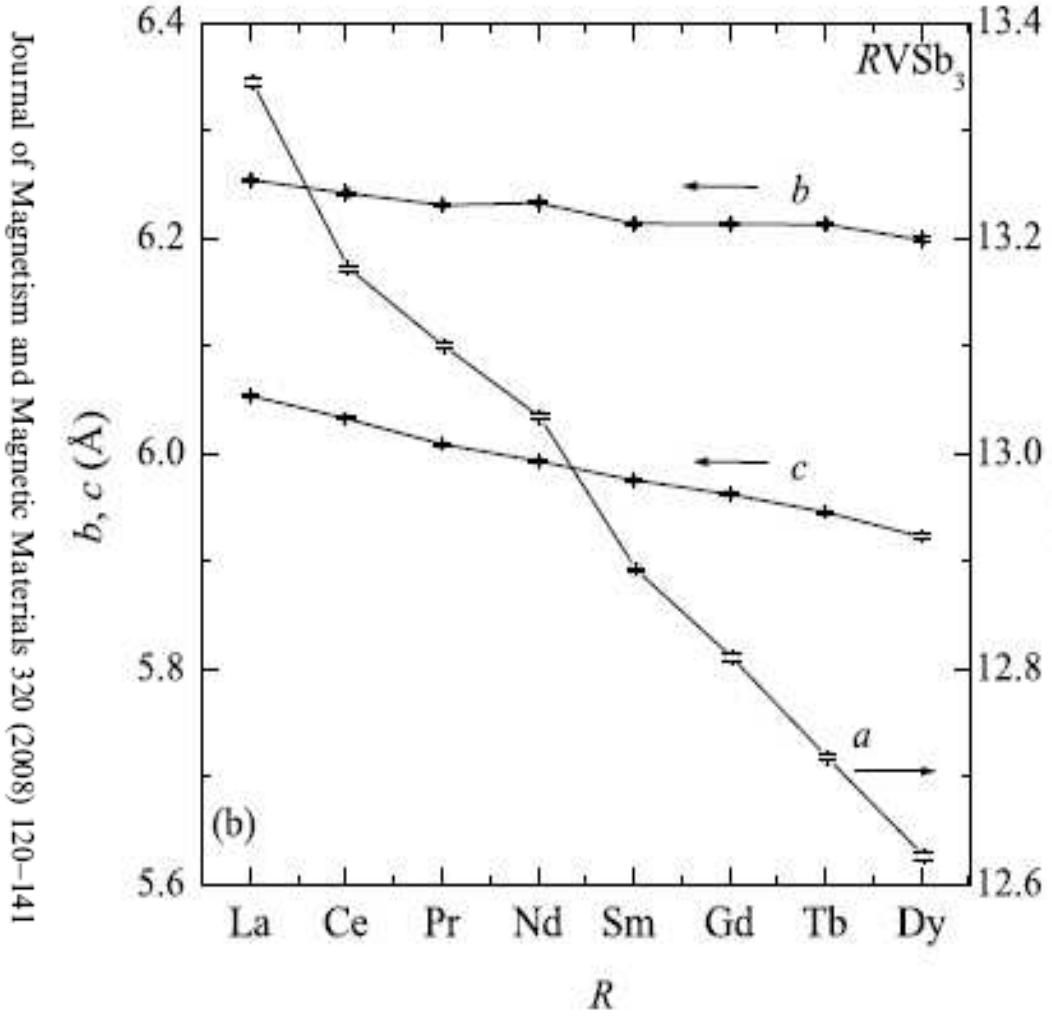
This contraction appears in the *volume* of the unit cell of isostructural $R^{3+}XY$ compounds. Note: (1) R^{2+}, R^{4+} deviate; (2) a, b, c variation can be different; and (3) Y usually appears near Dy.



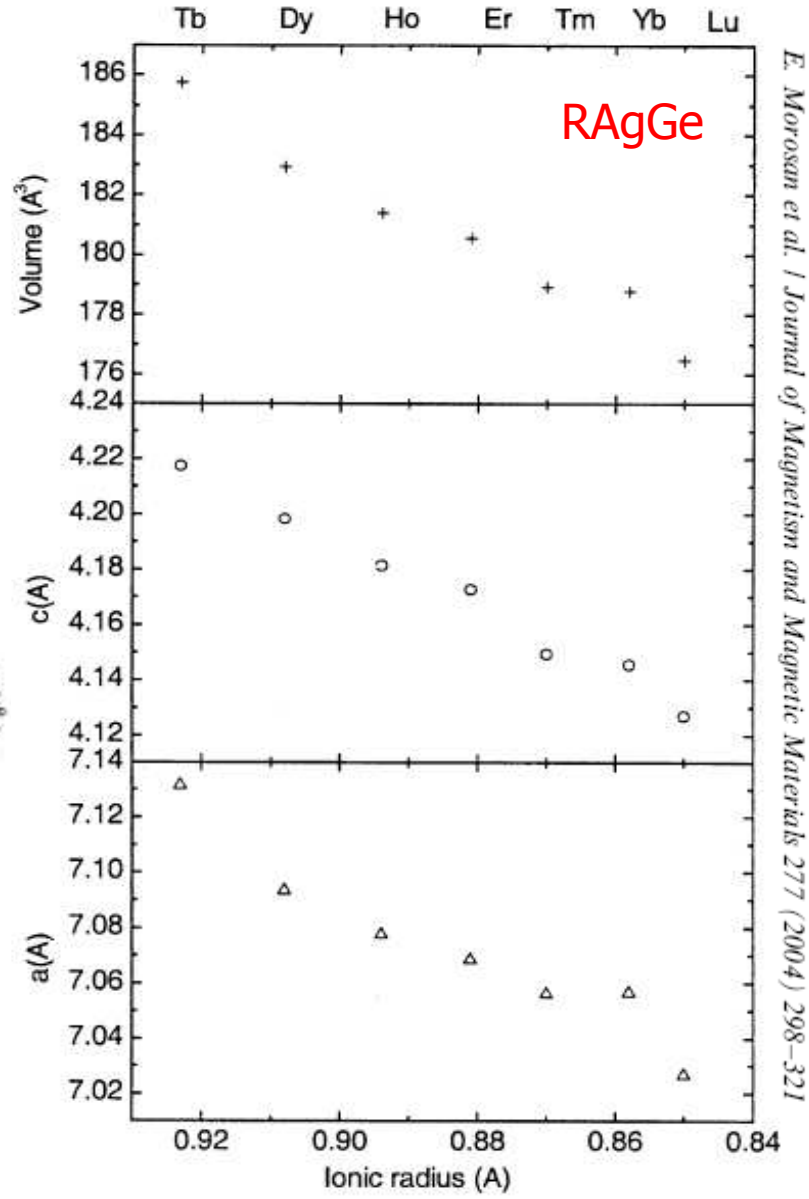


Handbook of crystal structures and magnetic properties of rare earth intermetallics by A. Szytula and J. Leciejewicz

In many RXY series R does not span the complete rare earth series. This is often associated with the lanthanide contraction bringing the unit cell parameters into / out of ranges of stability.



Journal of Magnetism and Magnetic Materials 320 (2008) 120–141



E. Morosan et al. / Journal of Magnetism and Magnetic Materials 277 (2004) 298–321

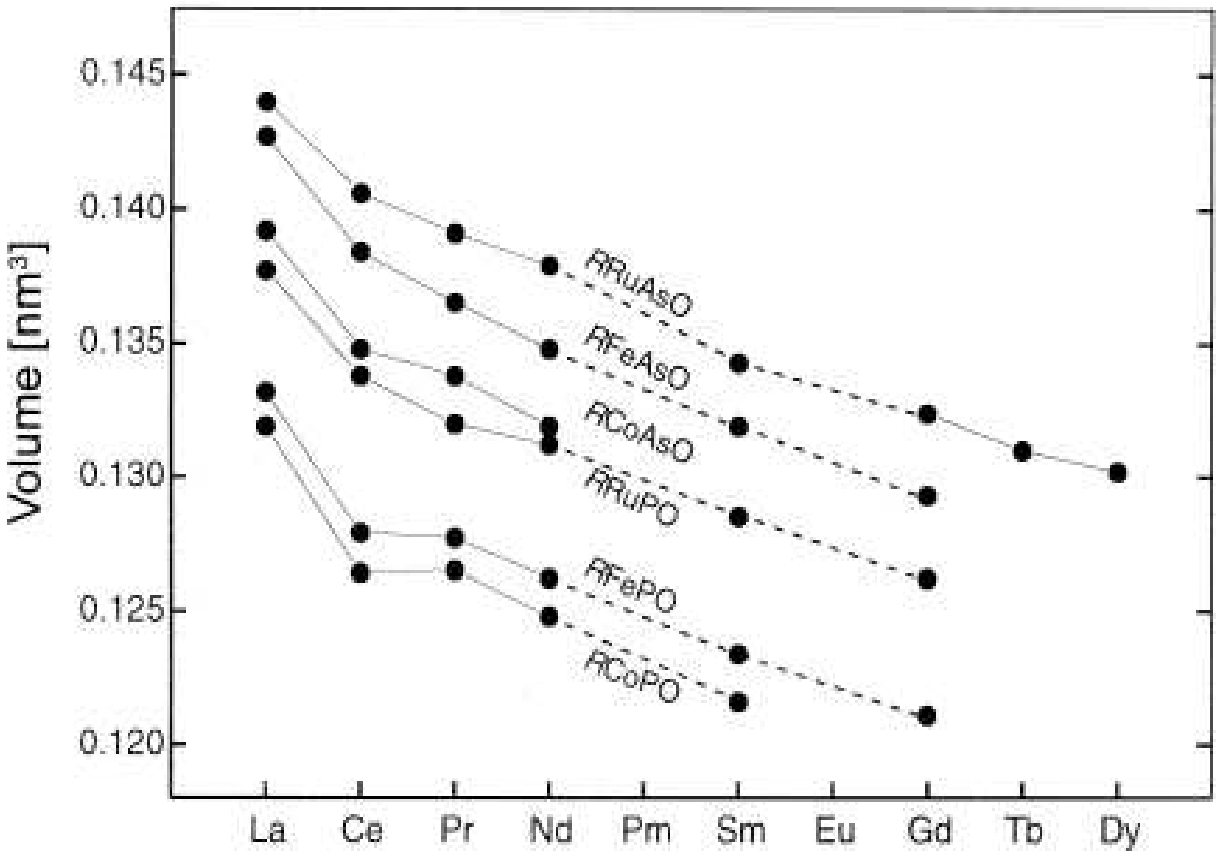
This contraction can often be thought of as a way of approximating either pressure or stress. This is particularly relevant in the current, very hot, topic of superconductivity in the $RFeAs(O_{1-x}F_x)$ compounds.

(1) For $x \sim 0.15$ and R = La superconductivity was found with $T_c \sim 30$ K

(2) Hydrostatic pressure of ~ 2 GPa (20 kbar) increased T_c to ~ 55 K

Subsequently it has been found that for $x \sim 0.15$ and R = Ce – Gd $T_c \sim 50 – 55$ K

For this series pressure and lanthanide contraction seem to stabilize the same superconducting ground state.



Journal of Alloys and Compounds 302 (2000) 70–74
P. Quebe, L.J. Terbüchte, W. Jeitschko

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Magnetization and susceptibility

The rare earth series really comes into its own when there is a need to tune magnetism. By controlling S, L, J we can get a wide variety of magnetic properties: μ_{eff}, μ_{sat} and coupling.

	f-shell ($l = 3$)										
	n	$l_z = 3,\ 2,\ 1,\ 0, -1, -2, -3$							S	$L = \lvert\Sigma l_z\rvert$	J	
Ce	1	↓							1/2	3	5/2	$^2F_{5/2}$
Pr	2	↓	↓						1	5	4	$^3H_4$
Nd	3	↓	↓	↓					3/2	6	9/2	$^4I_{9/2}$
Pm	4	↓	↓	↓	↓				2	6	4	$^5I_4$
Sm	5	↓	↓	↓	↓	↓			5/2	5	5/2	$^6H_{5/2}$
Eu	6	↓	↓	↓	↓	↓	↓		3	3	0	$^7F_0$
Gd	7	↓	↓	↓	↓	↓	↓	↓	7/2	0	7/2	$^8S_{7/2}$
Tb	8	↓↑	↑	↑	↑	↑	↑	↑	3	3	6	$^7F_6$
Dy	9	↓↑	↓↑	↑	↑	↑	↑	↑	5/2	5	15/2	$^6H_{15/2}$
Ho	10	↓↑	↓↑	↓↑	↑	↑	↑	↑	2	6	8	$^5I_8$
Er	11	↓↑	↓↑	↓↑	↓↑	↑	↑	↑	3/2	6	15/2	$^4I_{15/2}$
Tm	12	↓↑	↓↑	↓↑	↓↑	↓↑	↑	↑	1	5	6	$^3H_6$
Yb	13	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↑	1/2	3	7/2	$^2F_{7/2}$
Lu	14	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	0	0	0	$^1S_0$

$J = |L - S|$ (Ce–Eu); $J = L + S$ (Tb–Tm)

Ashcroft / Mermin Solid State Physics

Magnetization and susceptibility

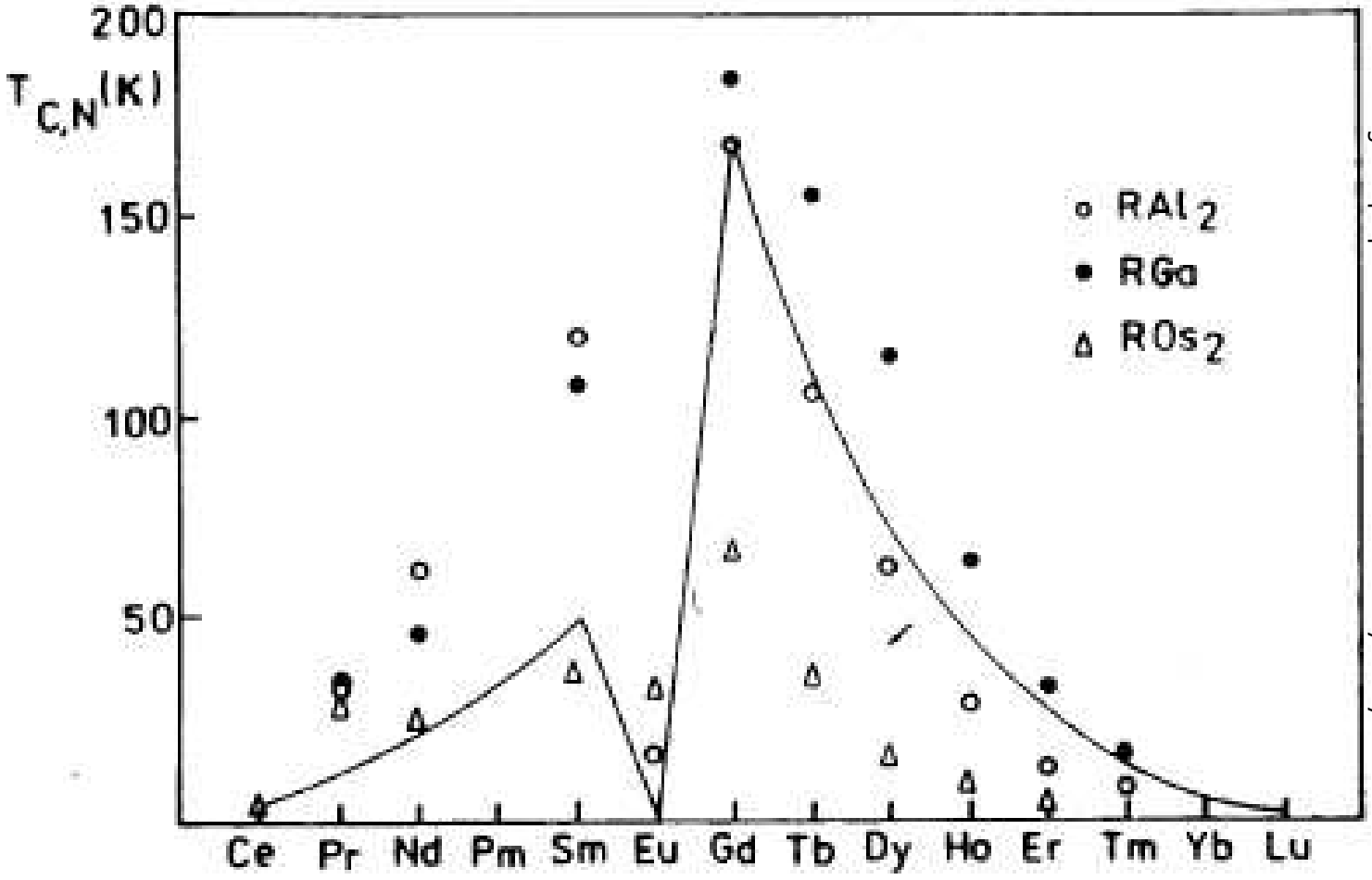
Table 1 Effective magneton numbers p for trivalent lanthanide group ions
(Near room temperature)

Kittel, Introduction to Solid State physics 4th edition

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{\frac{1}{2}}$	$p(\text{exp})$, approximate
Ce^{3+}	$4f^1 5s^2 p^6$	$^2F_{5/2}$	2.54	2.4
Pr^{3+}	$4f^2 5s^2 p^6$	$^3H_4$	3.58	3.5
Nd^{3+}	$4f^3 5s^2 p^6$	$^4I_{9/2}$	3.62	3.5
Pm^{3+}	$4f^4 5s^2 p^6$	$^5I_4$	2.68	—
Sm^{3+}	$4f^5 5s^2 p^6$	$^6H_{5/2}$	0.84	1.5
Eu^{3+}	$4f^6 5s^2 p^6$	$^7F_0$	0	3.4
Gd^{3+}	$4f^7 5s^2 p^6$	$^8S_{7/2}$	7.94	8.0
Tb^{3+}	$4f^8 5s^2 p^6$	$^7F_6$	9.72	9.5
Dy^{3+}	$4f^9 5s^2 p^6$	$^6H_{15/2}$	10.63	10.6
Ho^{3+}	$4f^{10} 5s^2 p^6$	$^5I_8$	10.60	10.4
Er^{3+}	$4f^{11} 5s^2 p^6$	$^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12} 5s^2 p^6$	$^3H_6$	7.57	7.3
Yb^{3+}	$4f^{13} 5s^2 p^6$	$^2F_{7/2}$	4.54	4.5

In addition to being able to vary S, L, J as well a μ_{eff} and μ_{sat}, by projecting the S·s interaction onto the total angular momentum, J, and using mean field theory we find that T_N = (Const.) * $(g_J-1)^2J(J+1)$.

$(g_J-1)^2J(J+1)$ is referred to as the de Gennes factor and is often denoted by dG.

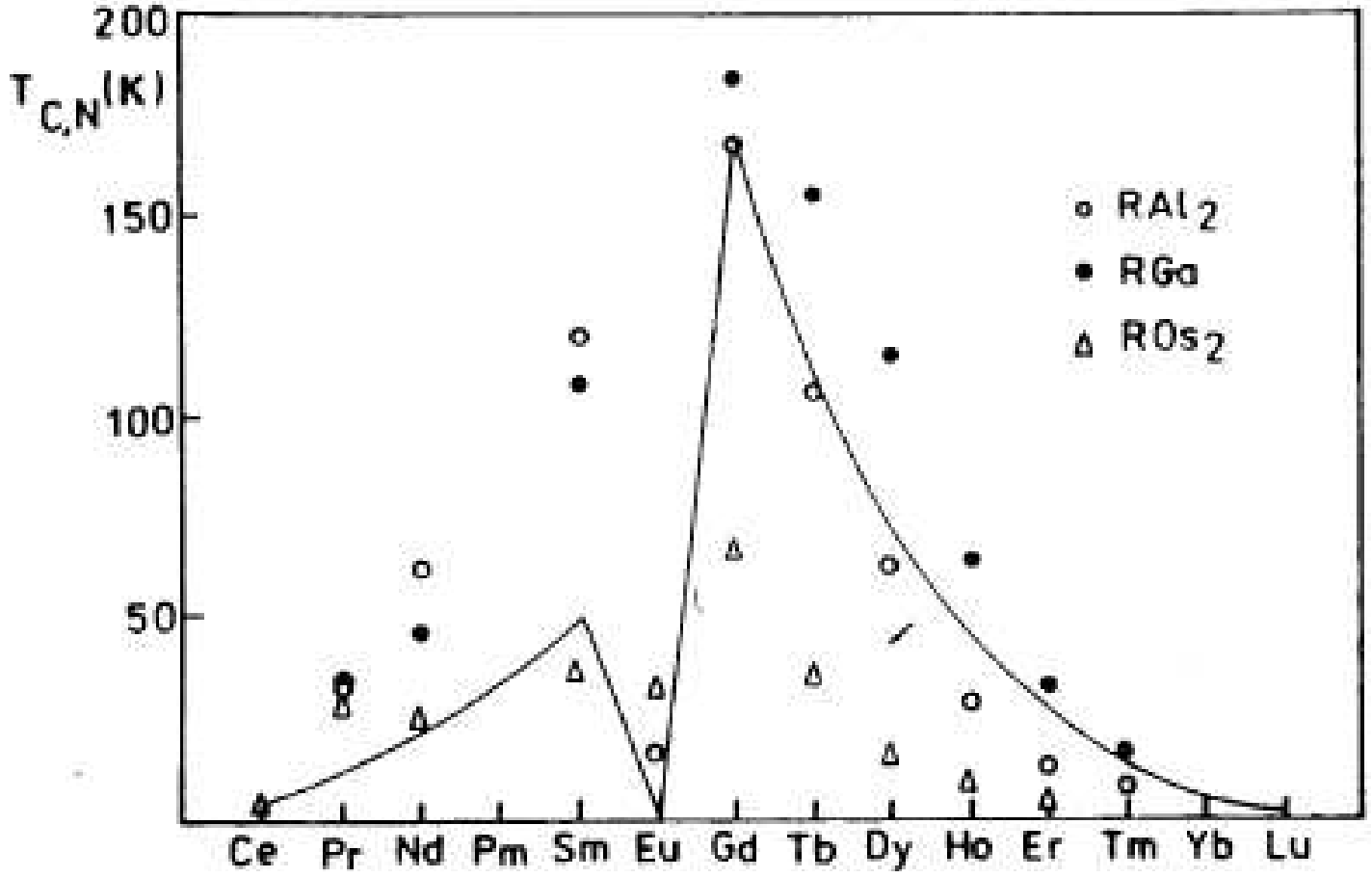


$$T_N = \frac{3\pi n^2}{k_B E_F} J_{sf}^2 (g_J - 1)^2 J(J+1) \sum_{i \neq 0} F(2k_F R_{Oi}) \cos(\vec{k}_O \cdot \vec{R}_{Oi})$$

Handbook of crystal structures and magnetic properties of rare earth intermetallics by A. Szytula and J. Leciejewicz

dG scaling clearly illustrates the difference between the light (La – Eu) and heavy (Gd – Lu) rare earths….

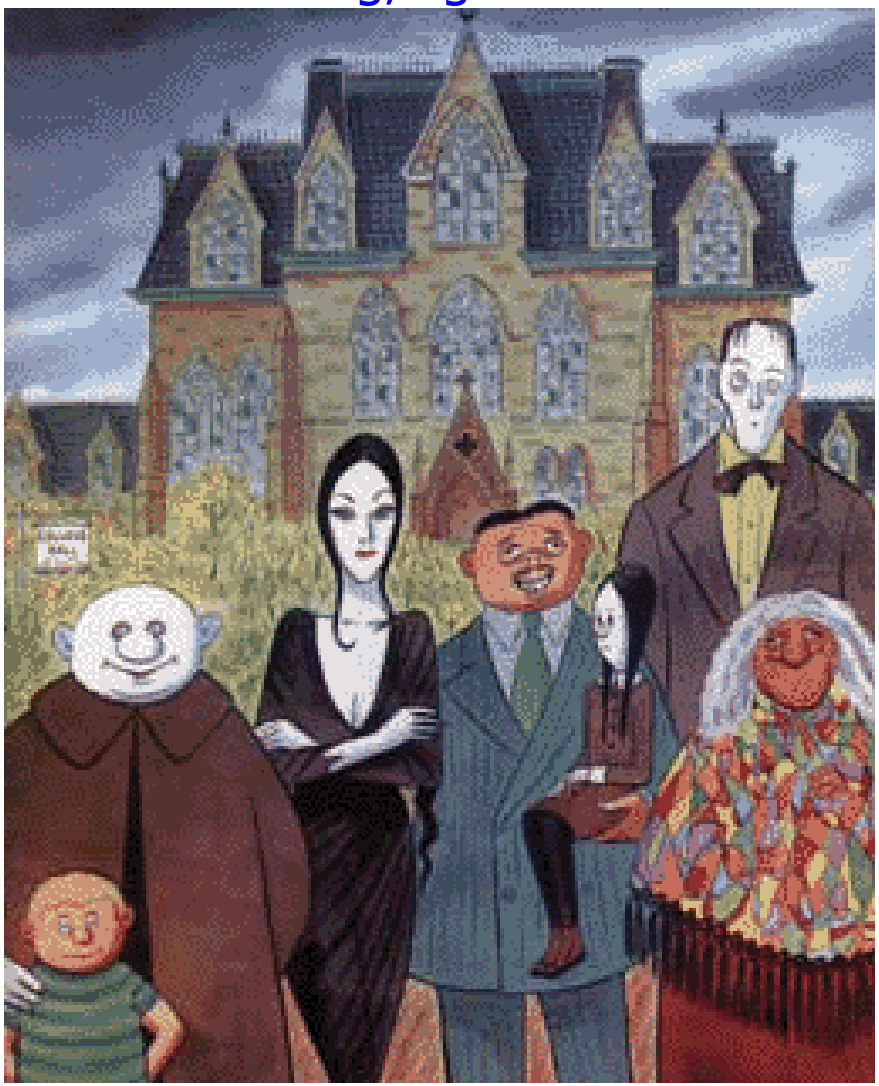
57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.9	140.1	140.9	144.2	146.9	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0
	XXX hyb	XXX sng	3+ OK	XXX HOT	XXX Hund	XXX div	3+ OK	3+ OK	3+ OK	3+ OK	3+ OK	3+ OK	XXX hyb



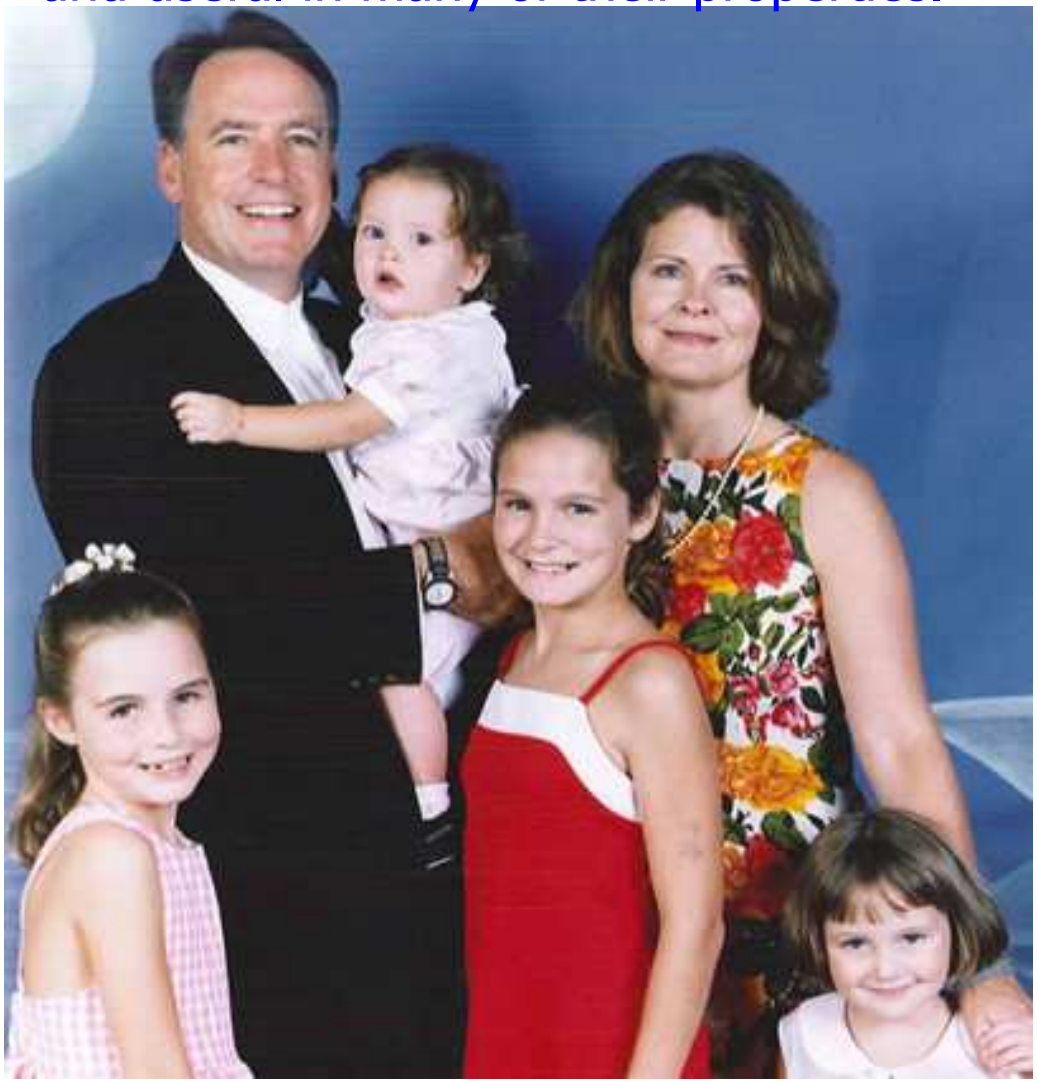
The light and heavy rare earths are like two different families

57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.9	140.1	140.9	144.2	146.9	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0

Poorly behaved, but interesting, lights

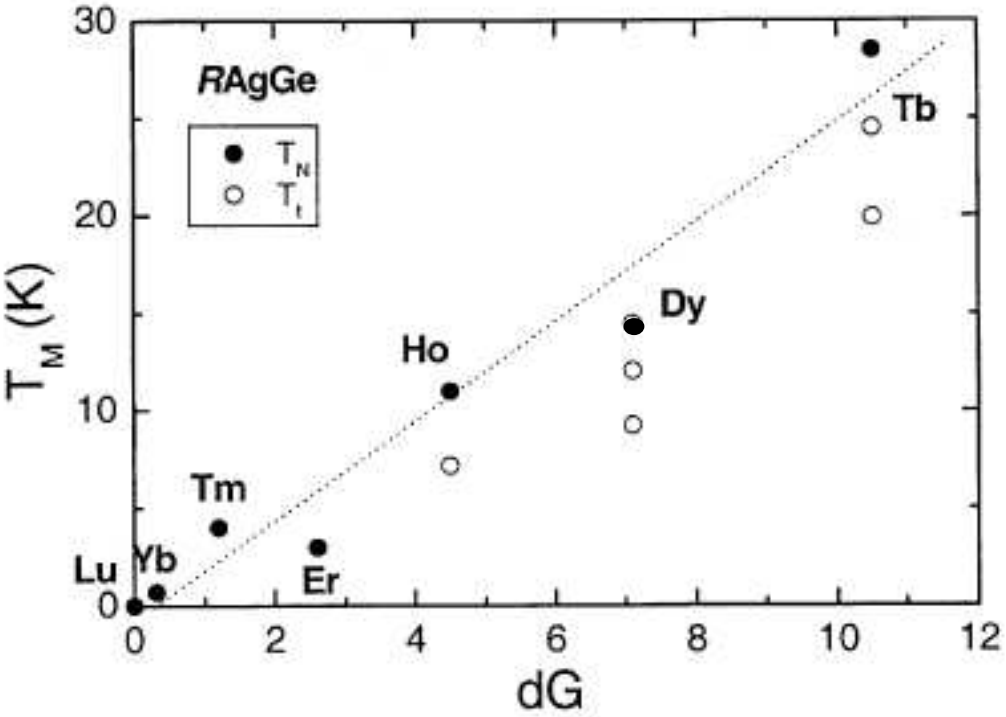


Well behaved heavies that are predicable and useful in many of their properties.



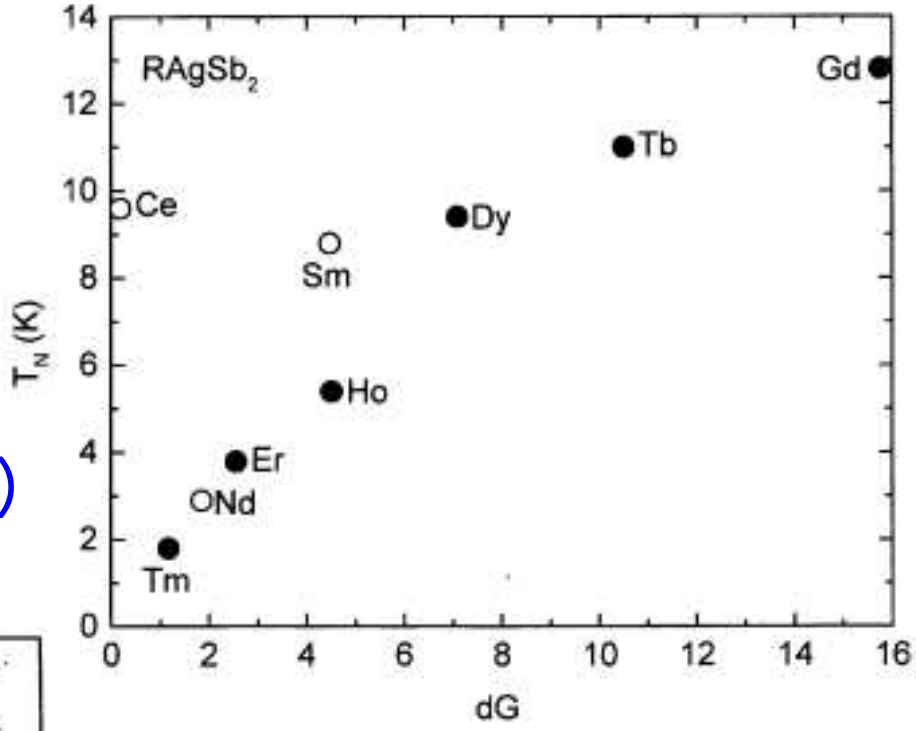
dG scaling can be used to control / predict ordering temperature, especially for R = heavy members.

For $RAgSb_2$ R = Nd is on dG line but other lights are off (as usual)



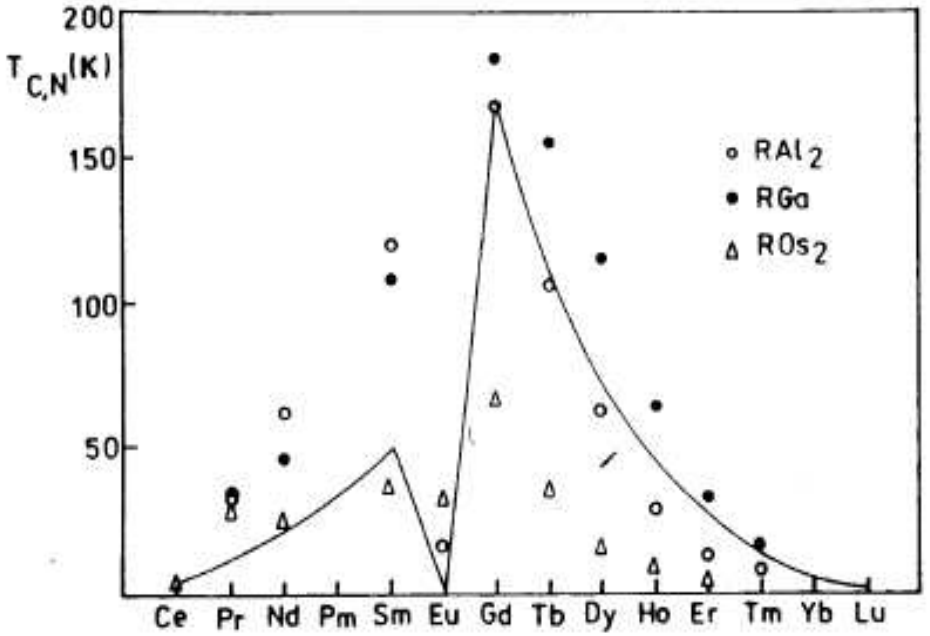
E. Morosan et al. / Journal of Magnetism and Magnetic Materials 277 (2004) 298–321

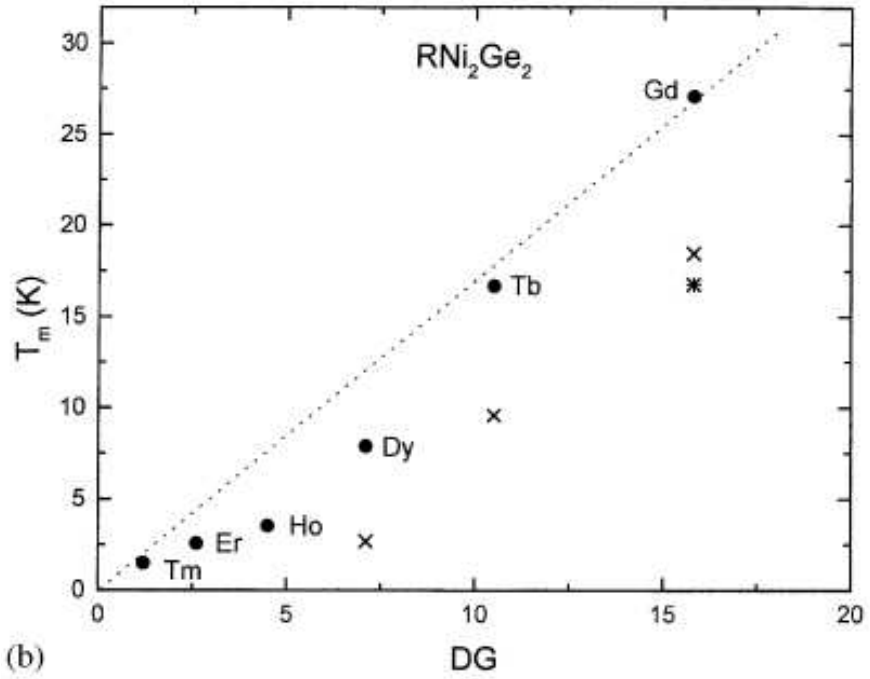
K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52

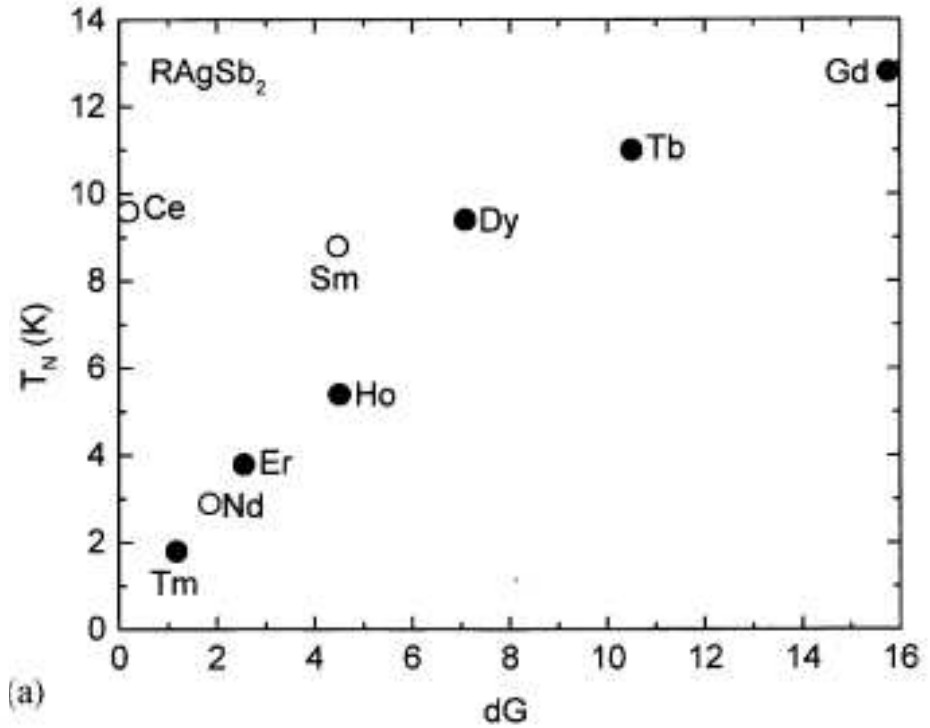


For RAgGe there is fair dG scaling even for lower temperature, order to order, transitions (often incommensurate to commensurate long range order).

Since dG scaling predicts the R = Gd member of a series with have the highest ordering temperature (and Gd is well behaved), Gd-members of RXY series can be used as litmus tests for strength of ordering….



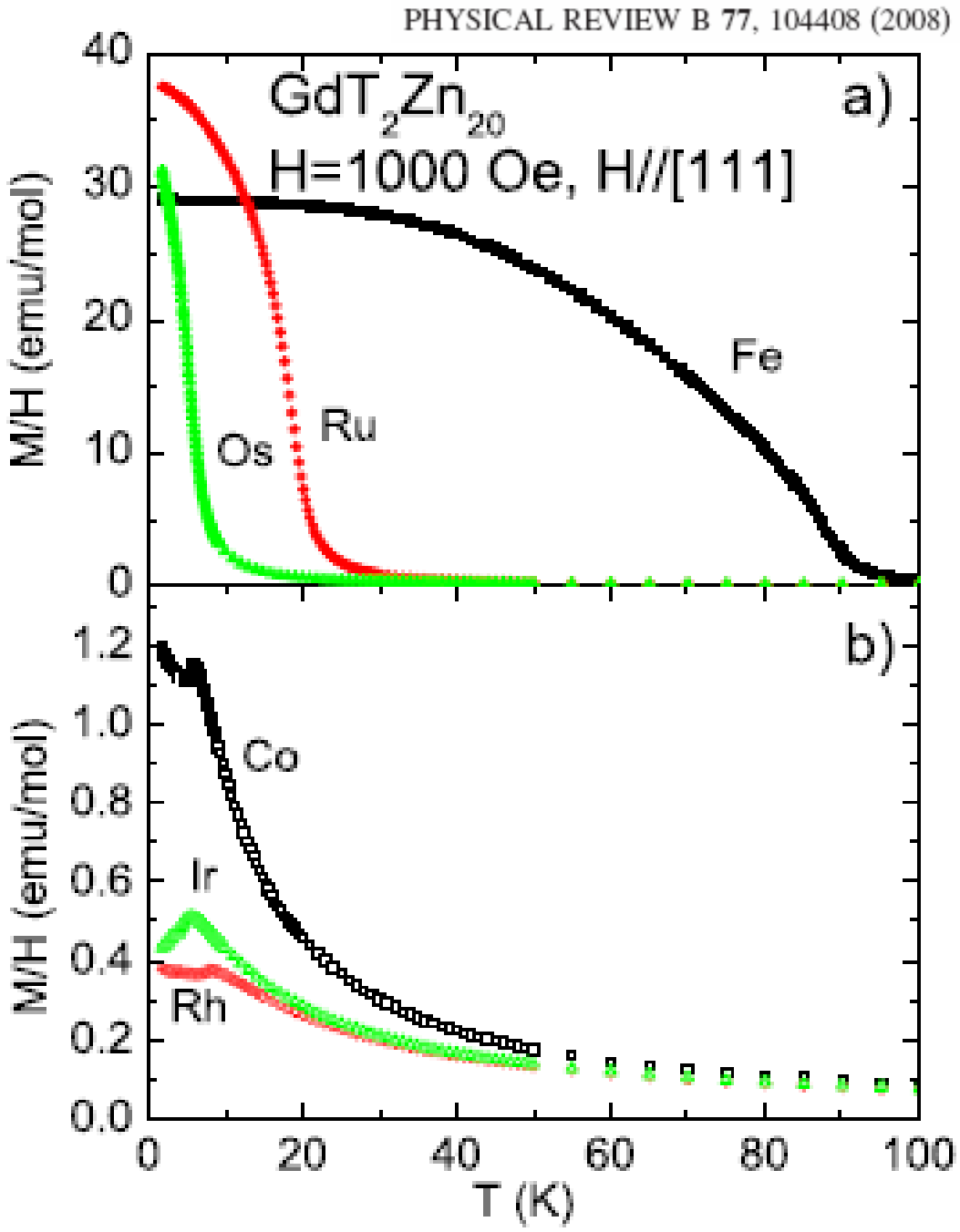




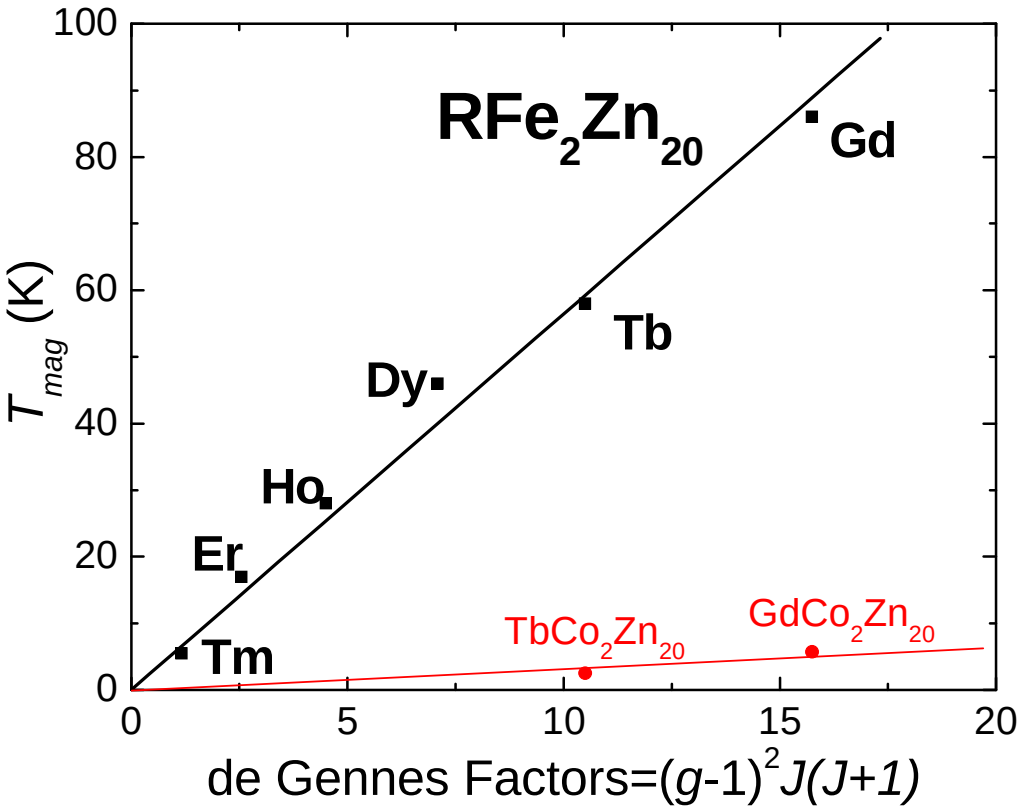
S.L. Bud'ko et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 53–78

K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52

In our recent work on the dilute, rare earth bearing, intermetallic compounds RT_2Zn_{20} we used the six GdT_2Zn_{20} compounds to give us a caliper of how strong (and what type) or ordering we could expect from the respective series.



As can be seen, R= Gd is not special: The whole RFe_2Zn_{20} series has enhanced T_C values that de Gennes scale well.



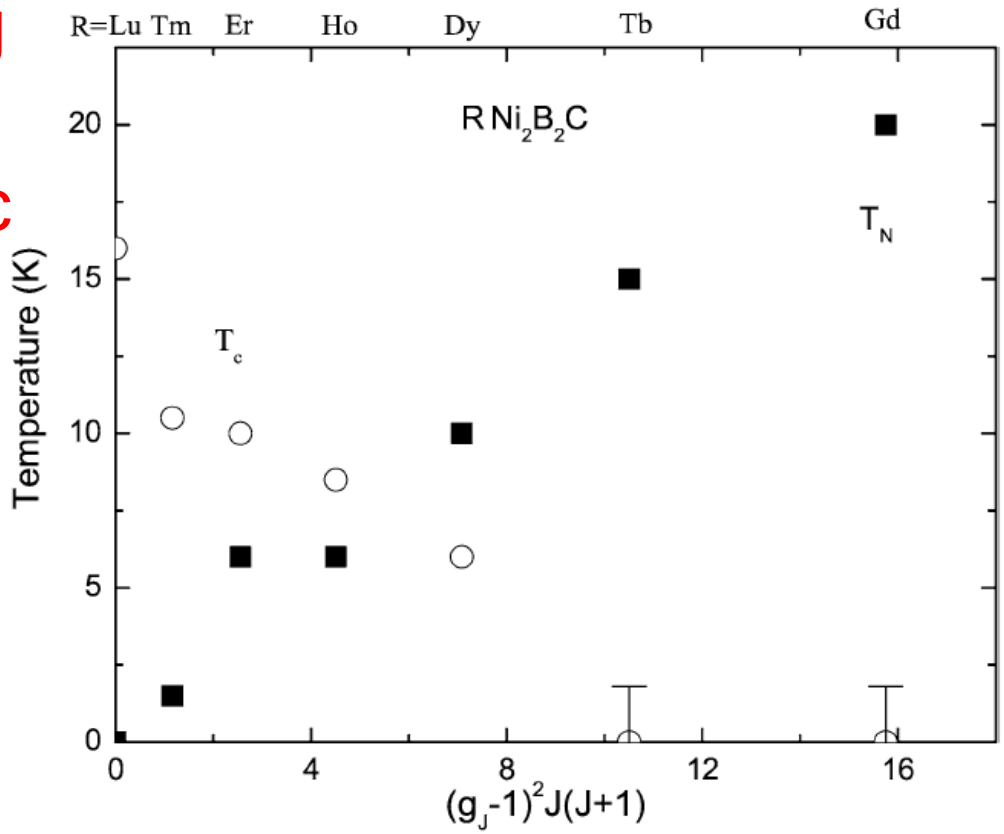
The question is, "Why does the RFe_2Zn_{20} series manifest such high ordering temperatures?"

The answer is Stoner enhancement of the conduction electrons matrix, e.g. YFe_2Zn_{20} is closer to the Stoner limit than Pd.

P. C. Canfield et al. Physics Today Oct. 1998

Very clear dG scaling of T_N can be seen in the RNi_2B_2C family of magnetic superconductors.

In the paramagnetic state, the suppression of T_c is also proportional to the S·s coupling: the dG factor.



Superconducting for R = Dy, Ho, Er, Tm, Lu, Y with T_C values ranging from 17 K – 6 K

Magnetic order for R = Gd, Tb, Dy, Ho, Er, Tm with T_N values ranging from 20 K to 1.5 K

More about this tomorrow.

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The CEF splitting or $T_{\Delta CEF}$

The Kondo temperature T_K

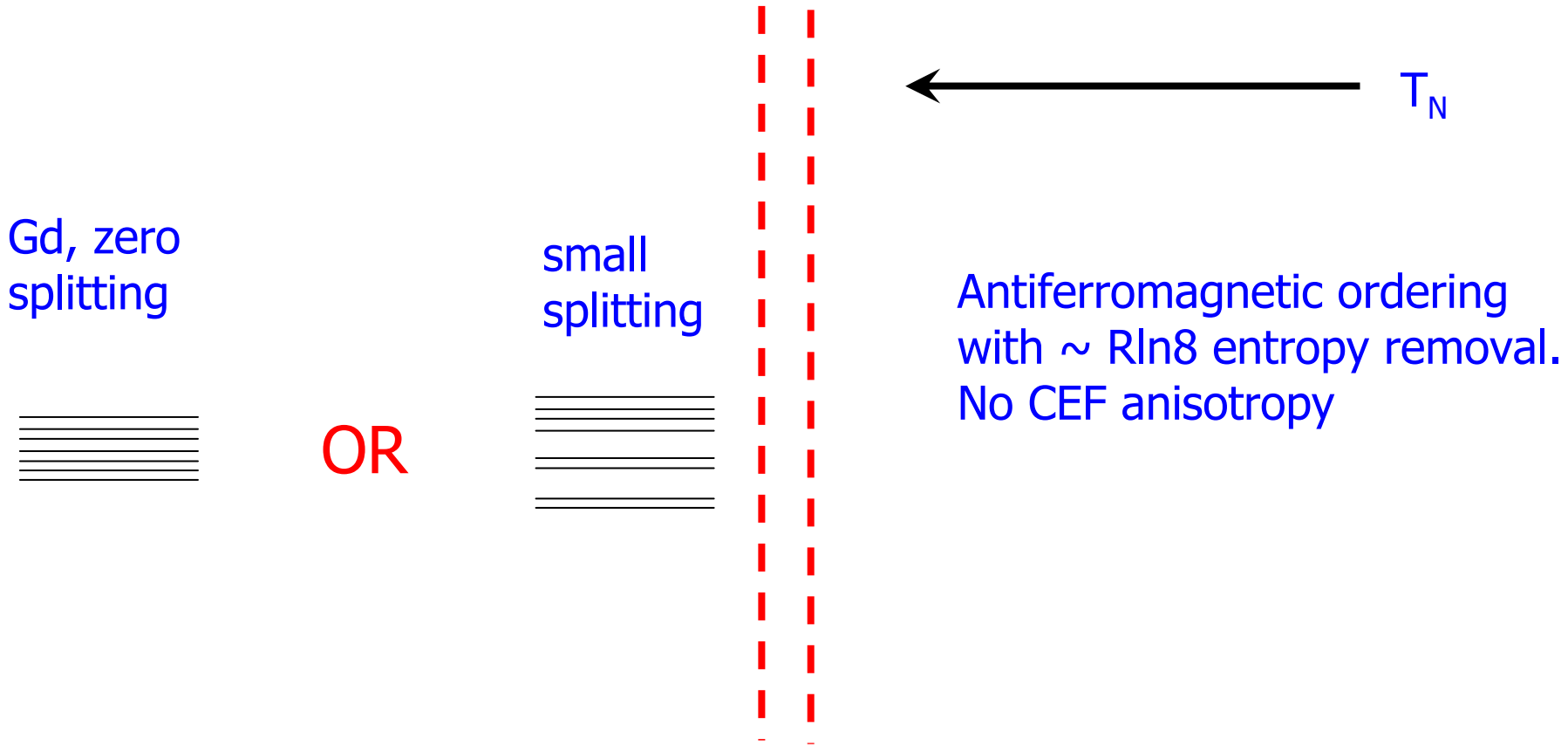
The Hund's rule goundstate multiplet, J, can be split by the crystal electric field that the rare earth ion finds itself in (associated with the point symmetry of the R ion and the details of its ligands). The CEF splitting determines (i) anisotropy and (ii) entropy, associated with 4f electrons, at a given temperature.

	n	$l_z = 3, \ 2, \ 1, \ 0, -1, -2, -3$	S	$L = \lvert\Sigma l_z\rvert$	J	
Ce	1	$\downarrow$	1/2	3	5/2	$^2F_{5/2}$
Pr	2	$\downarrow \ \downarrow$	1	5	4	$^3H_4$
Nd	3	$\downarrow \ \downarrow \ \downarrow$	3/2	6	9/2	$^4I_{9/2}$
Pm	4	$\downarrow \ \downarrow \ \downarrow \ \downarrow$	2	6	4	$^5I_4$
Sm	5	$\downarrow \ \downarrow \ \downarrow \ \downarrow \ \downarrow$	5/2	5	5/2	$^6H_{5/2}$
Eu	6	$\downarrow \ \downarrow \ \downarrow \ \downarrow \ \downarrow \ \downarrow$	3	3	0	$^7F_0$
Gd	7	$\downarrow \ \downarrow \ \downarrow \ \downarrow \ \downarrow \ \downarrow \ \downarrow$	7/2	0	7/2	$^8S_{7/2}$
Tb	8	$\updownarrow \ \uparrow \ \uparrow \ \uparrow \ \uparrow \ \uparrow \ \uparrow$	3	3	6	$^7F_6$
Dy	9	$\updownarrow \ \updownarrow \ \uparrow \ \uparrow \ \uparrow \ \uparrow \ \uparrow$	5/2	5	15/2	$^6H_{15/2}$
Ho	10	$\updownarrow \ \updownarrow \ \updownarrow \ \uparrow \ \uparrow \ \uparrow \ \uparrow$	2	6	8	$^5I_8$
Er	11	$\updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \uparrow \ \uparrow \ \uparrow$	3/2	6	15/2	$^4I_{15/2}$
Tm	12	$\updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \uparrow \ \uparrow$	1	5	6	$^3H_6$
Yb	13	$\updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \uparrow$	1/2	3	7/2	$^2F_{7/2}$
Lu	14	$\updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \updownarrow \ \updownarrow$	0	0	0	$^1S_0$

$J = |L - S|$ (Ce, Pr, Nd, Pm, Sm, Eu) $\quad J = L + S$ (Tb, Dy, Ho, Er, Tm, Yb)

Ashcroft / Mermin Solid State Physics

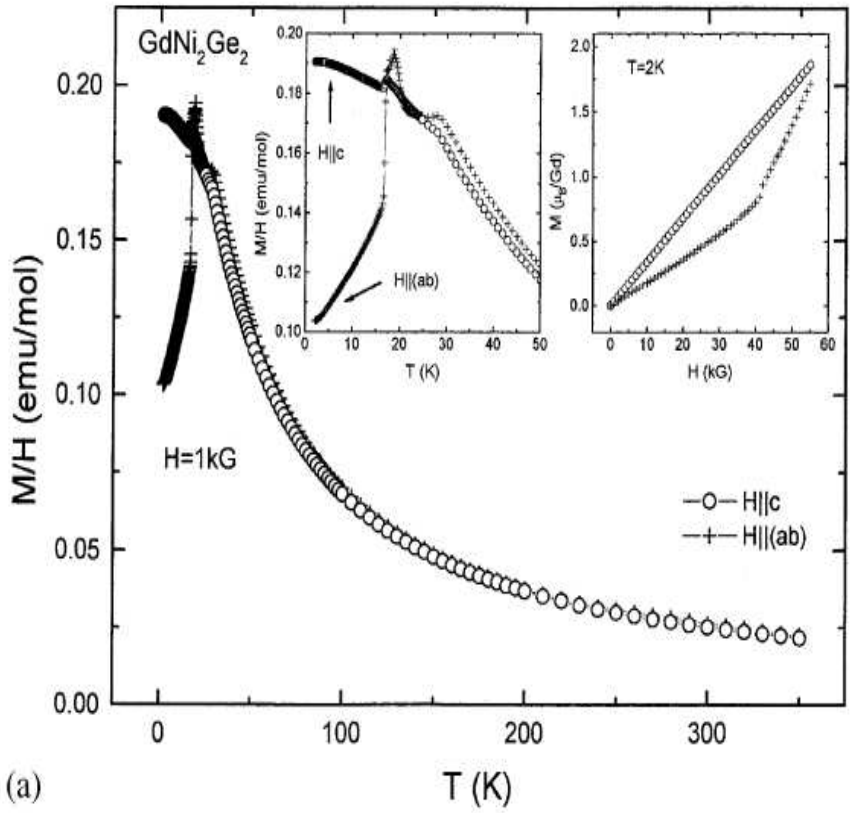
For Gd^{3+} or Eu^{2+} (L = 0), where there is formally zero CEF splitting, or for very small CEF splitting, T_N can be well above $T_{\Delta CEF}$. In these cases the local moment will be isotropic and full entropy will be removed through ordering.

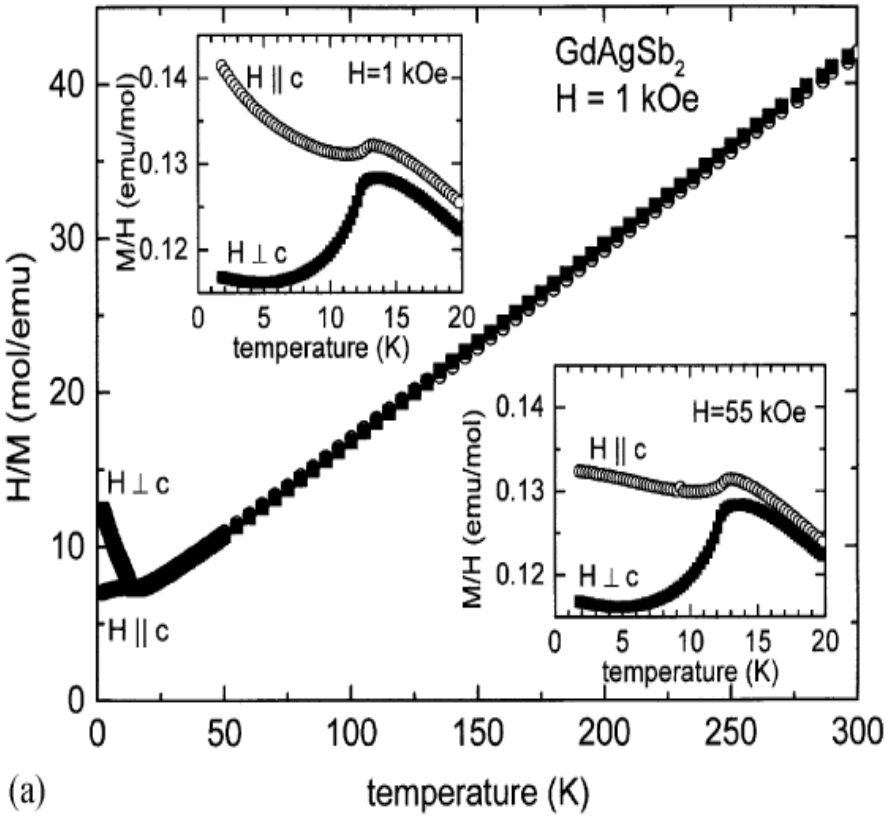


Gd members of RXY series will be isotropic

Gd offers a model Heisenberg moment

(this is one theoretical limit of treating moments simply)

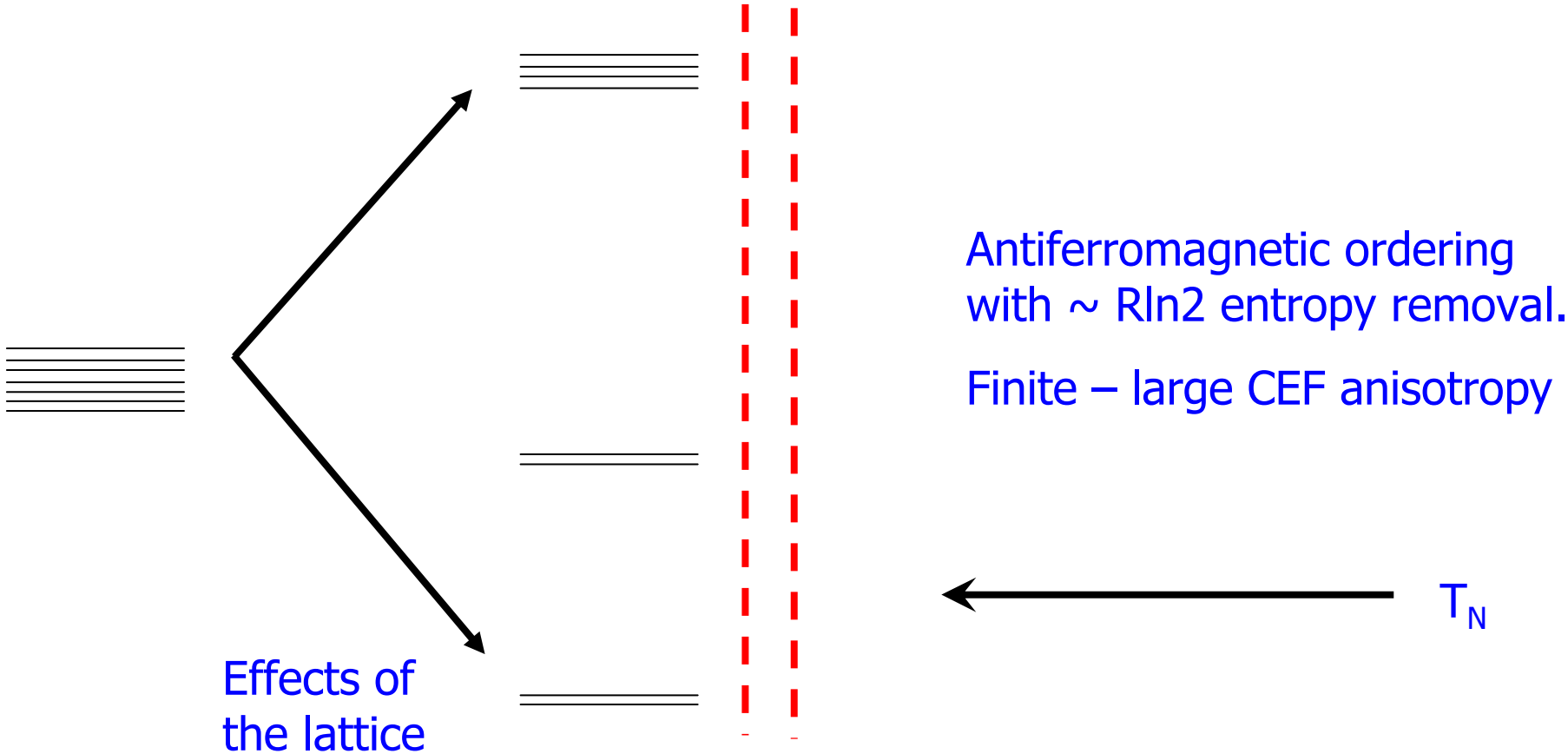




K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52

S.L. Bud'ko et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 53–78

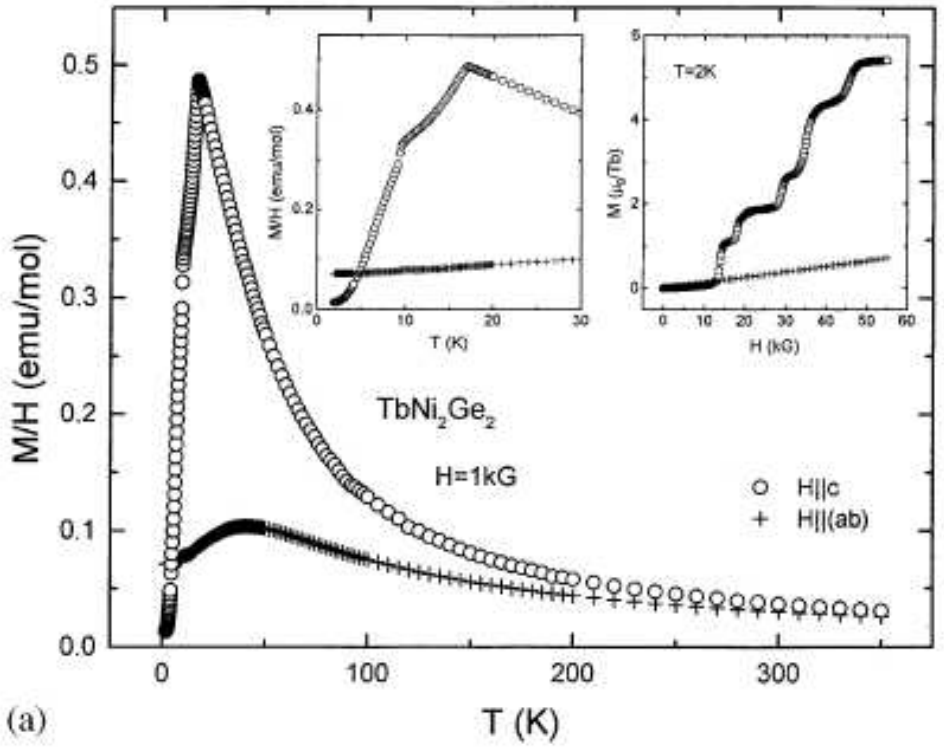
For rare earths with finite J and L ≠ 0 (i.e. not Gd^{3+} or Eu^{2+}) there will be CEF splitting of the Hund's rule ground state multiplet, J.

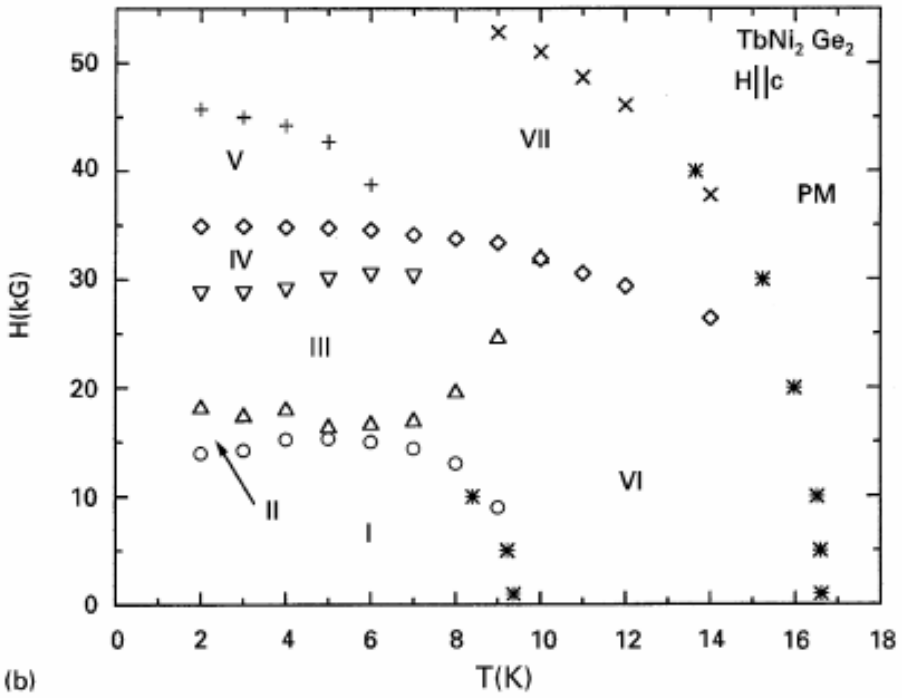


CEF anisotropy can be extreme, giving rise to the possibility of creating systems that approach the theoretical, ideally anisotropic moments.

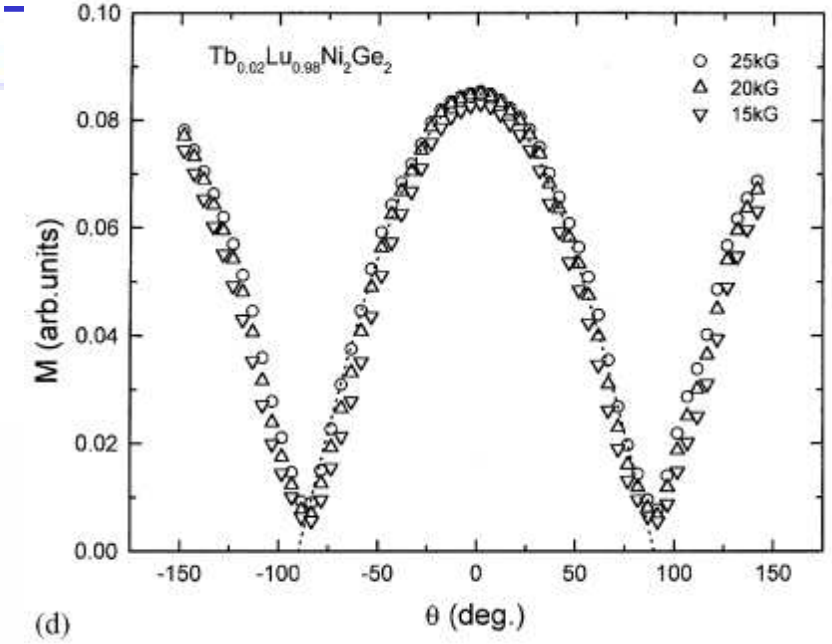
$TbNi_2Ge_2$

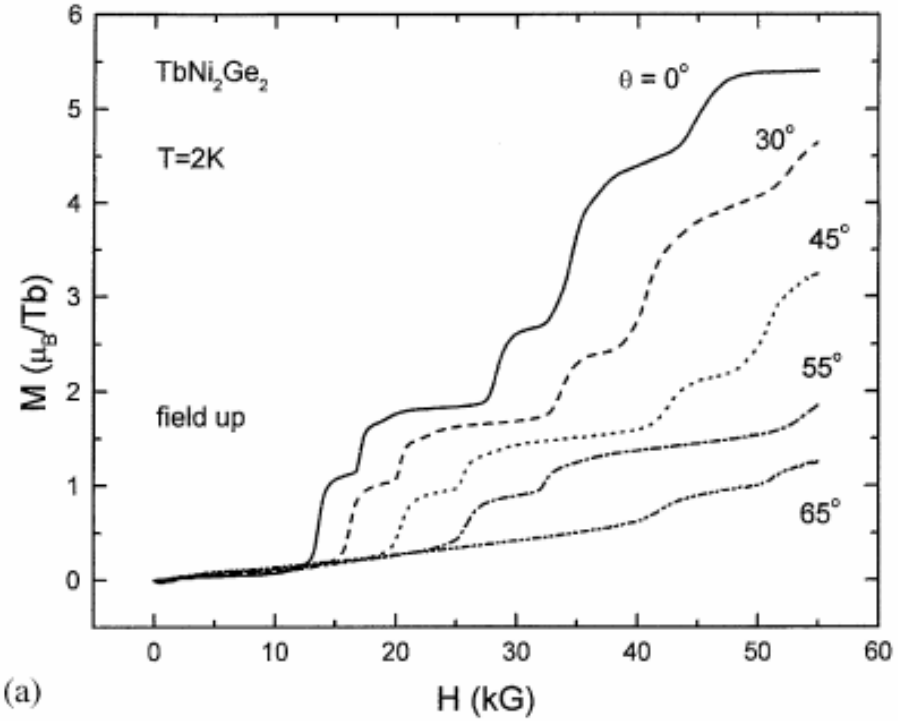
Tetragonal point symmetry of Tb site leads to Ising-like moment at low temperatures, **i.e. the local moment only points up or down along the c-axis**

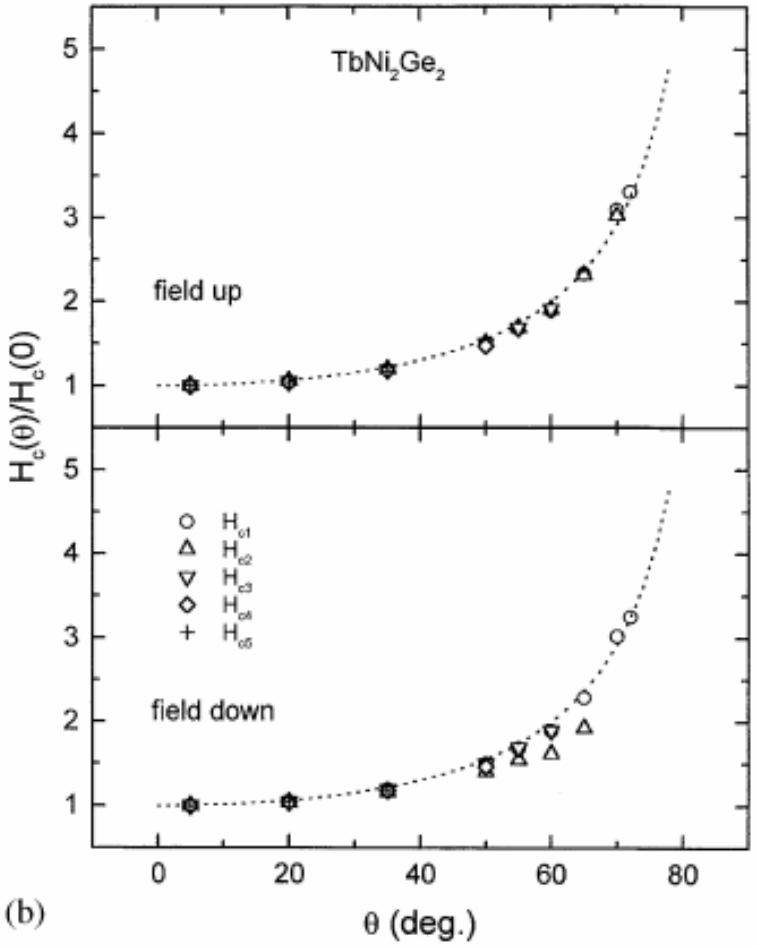




The applied magnetic field can be rotated away from the Ising axis and the metamagnetic transitions scale simply as 1/cosθ.







It should be noted that this axial anisotropy is not only of interest to physicists interested in extreme examples of Ising systems.

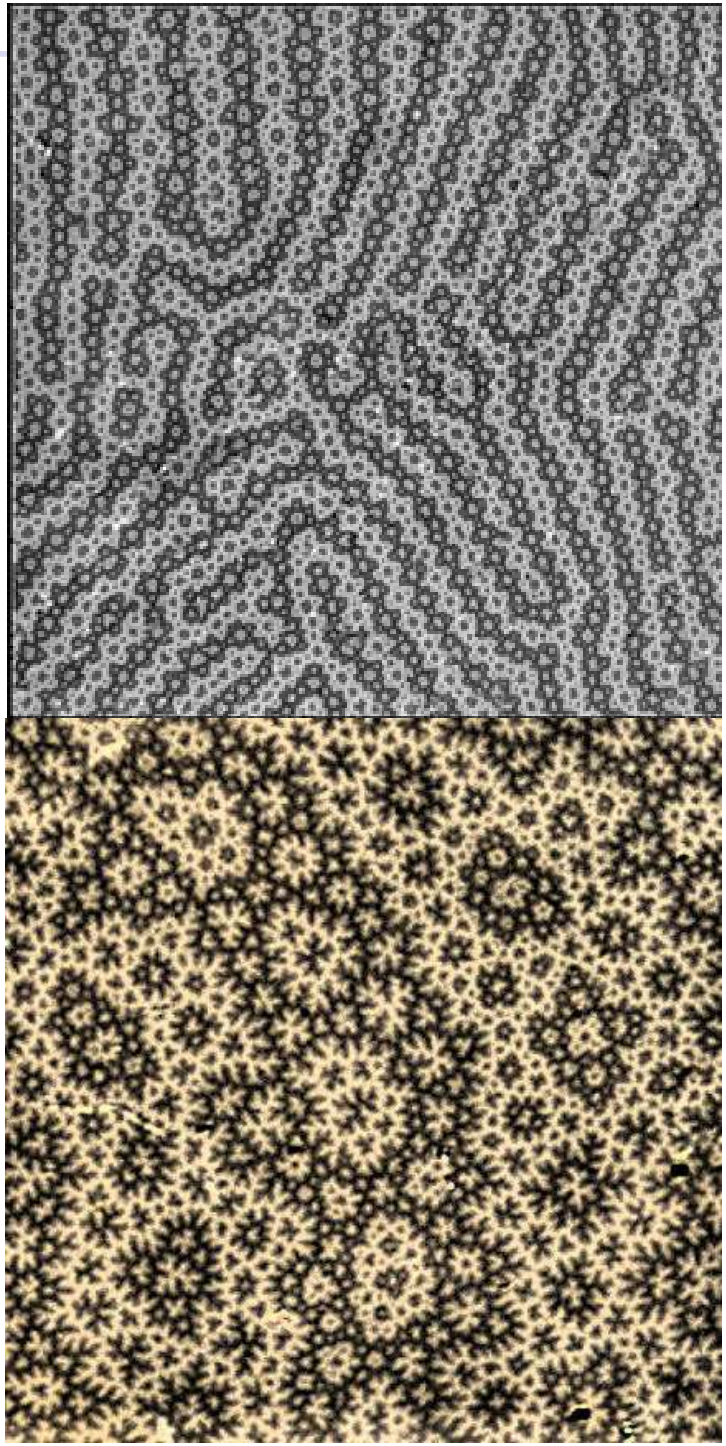
When the rare earth local moment is combined with transition metal (band) magnetism, the local moment can make the whole compound highly anisotropic.

$Nd_2Fe_{14}B$ is a case in point.

The well-behaved Nd ion provides an axial (Ising-like) ansiotropy to the compound that makes it the industrial ferromagnetic of choice.

It is worth noting that even such an applied material is of current interest to basic research. We have found a fractal-like nature of the magnetic domains in high purity, near zero pinning, single crystals.

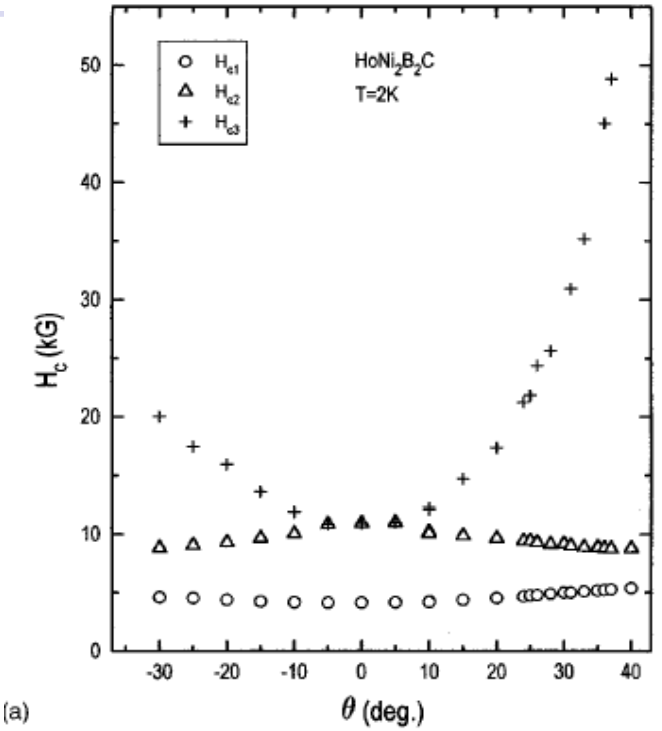
A. Kreyssig, R. Prozorov et al., in preparation

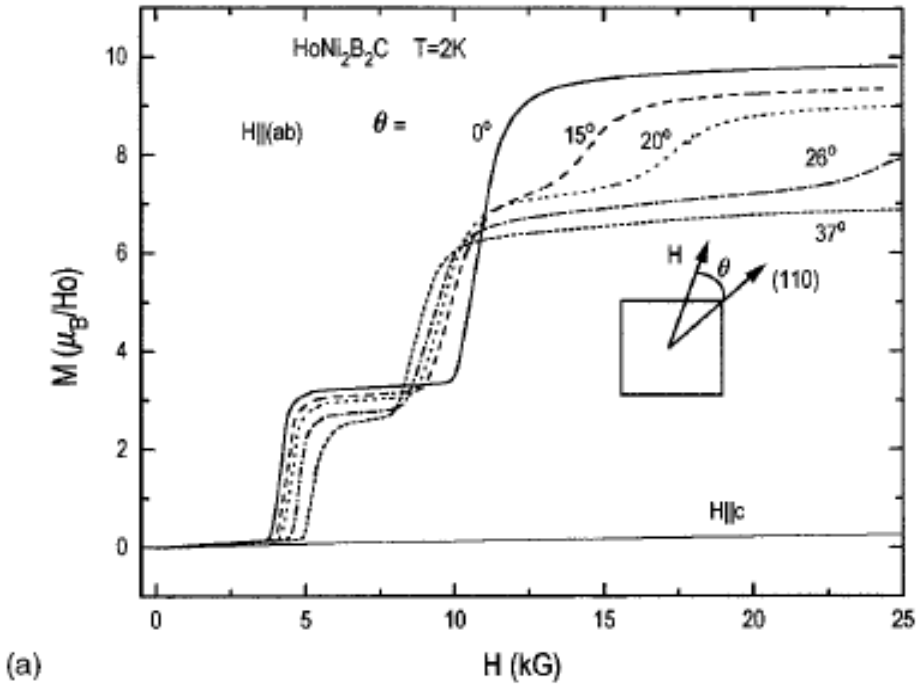


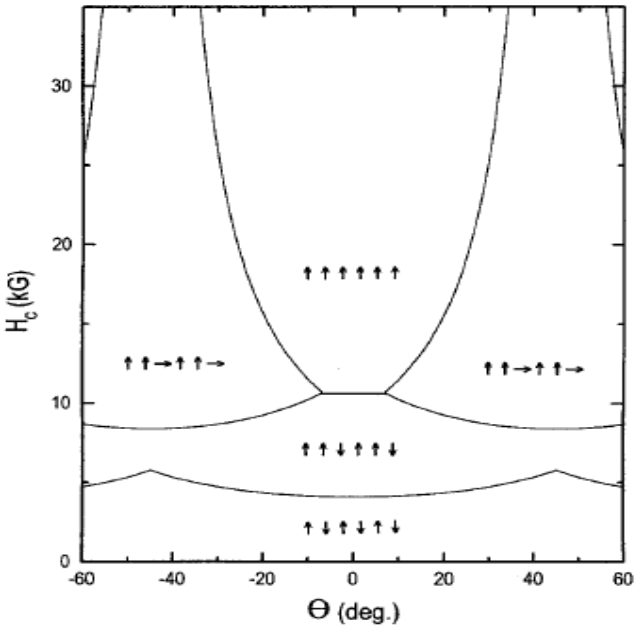
More complex, well defined, anisotropies:

4-state clock model in $HoNi_2B_2C$

In the case of $HoNi_2B_2C$ we were able to determine that the CEF splitting confines the moments to the basal plane along the 110 directions, leading to a 4-state clock model type of system.



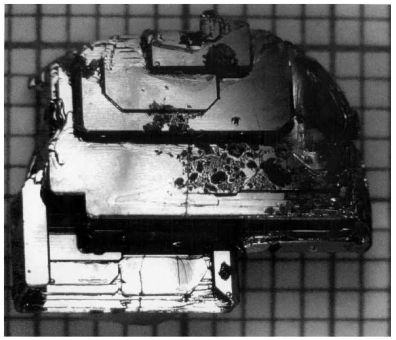




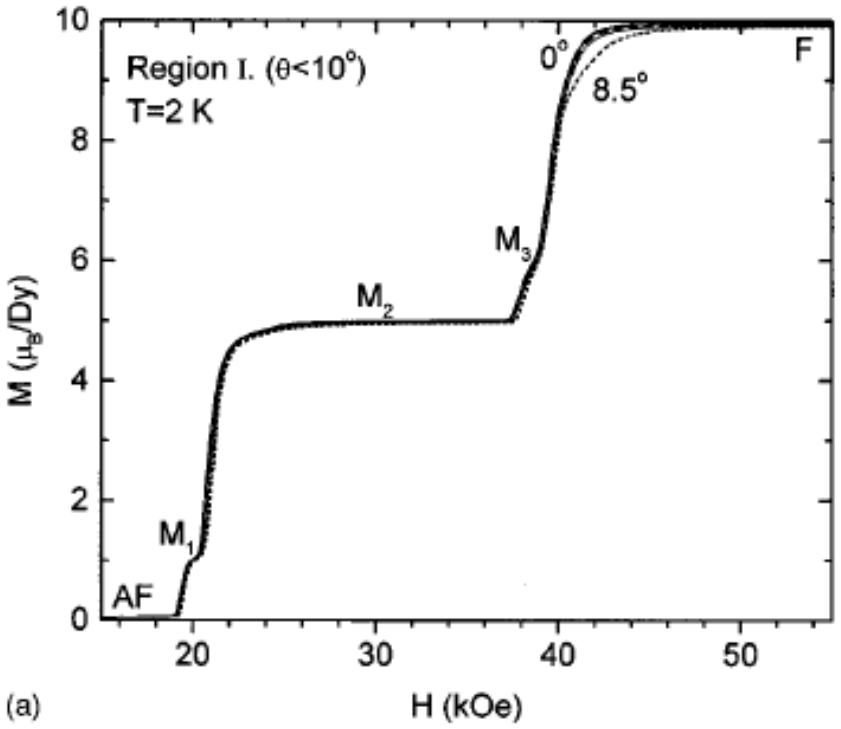
The realization that rare earth anisotropy could give rise to in-plane anisotropy shocked some groups (there was a belief that the moments would have xy isotropy). In order to show that this was a generalizable discovery….

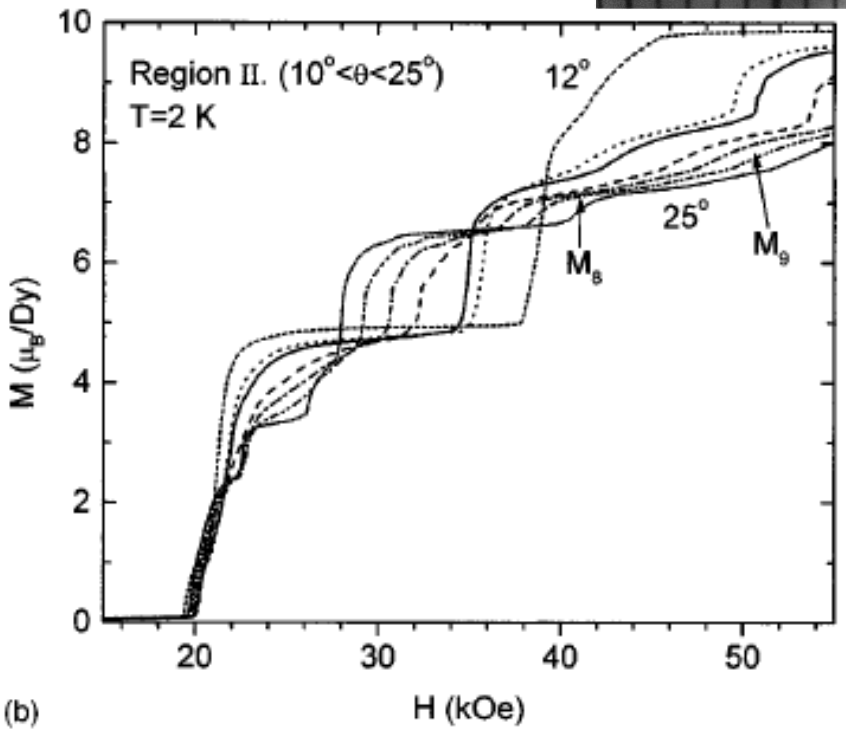
We searched for a different crystal structure class with a single R in a tetragonal point symmetry and found similar physics in

$DyAgSb_2$



~1 g crystal of $LaAgSb_2$

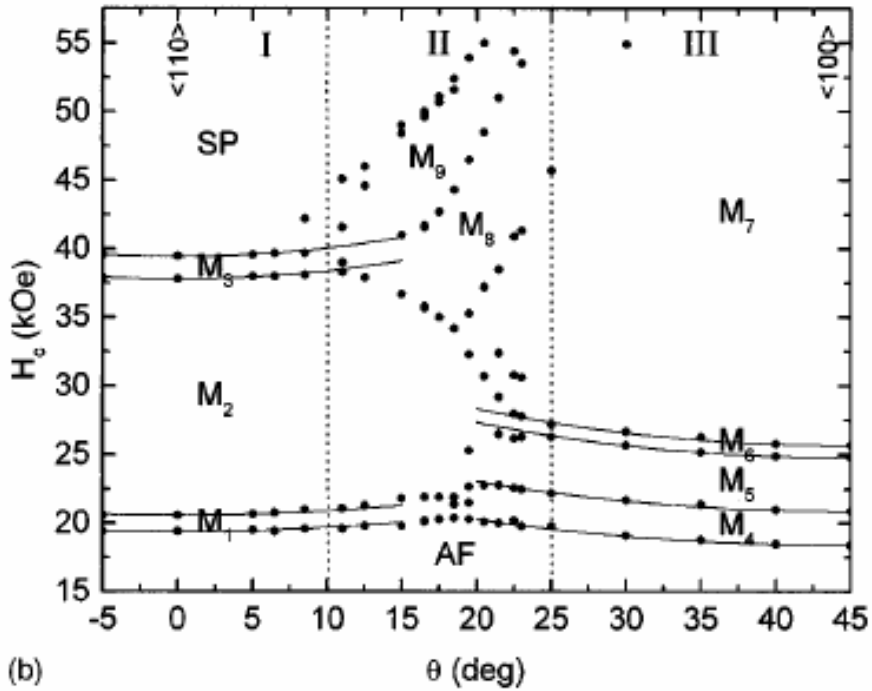


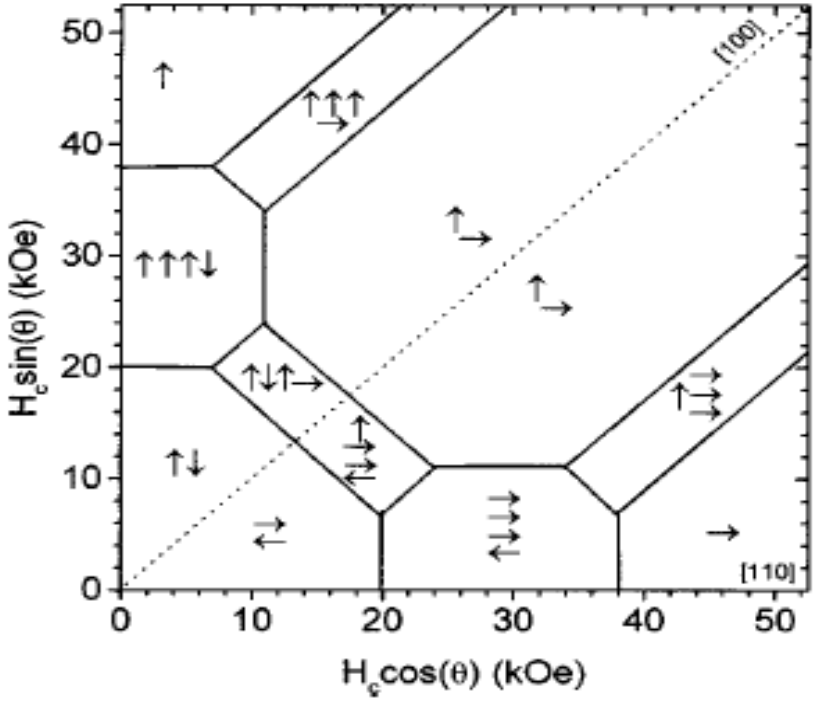


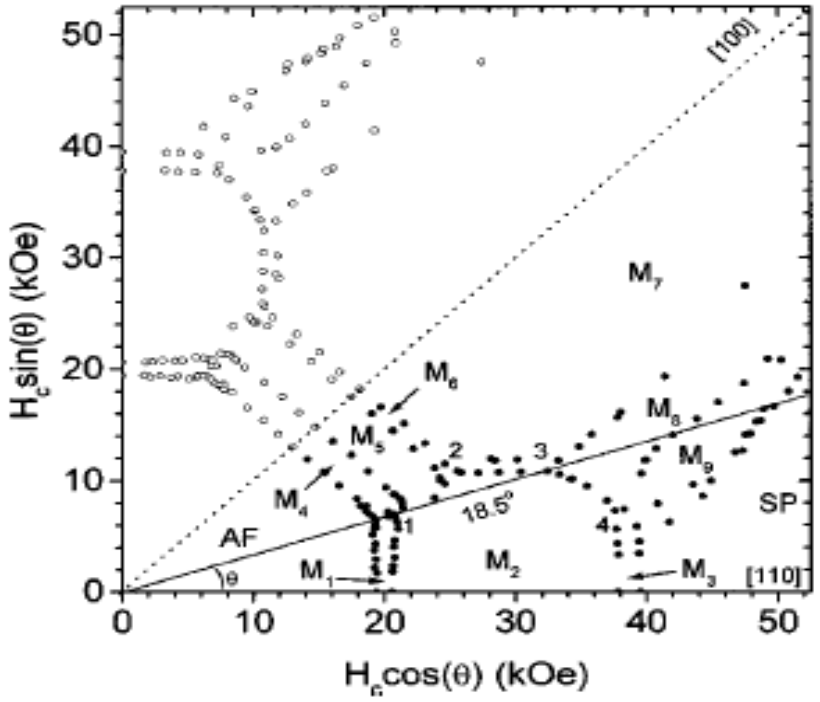
$DyAgSb_2$

The angular dependent magnetization data can be used to assemble a rich and complex phase diagram….

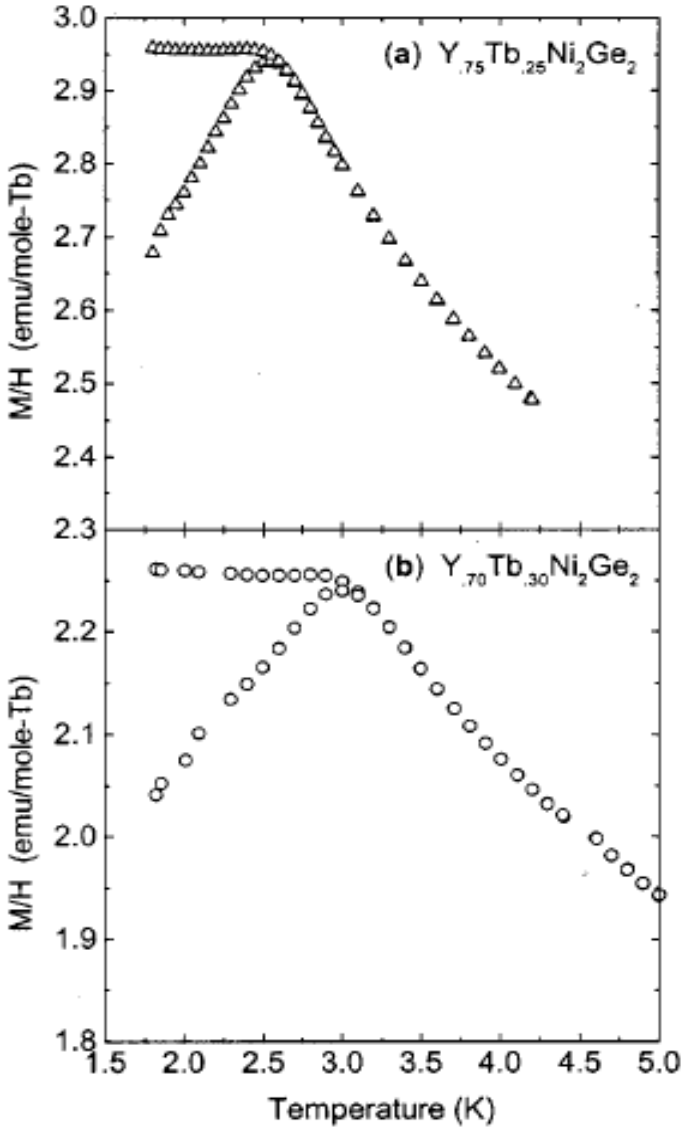
of a 4-state clock model system





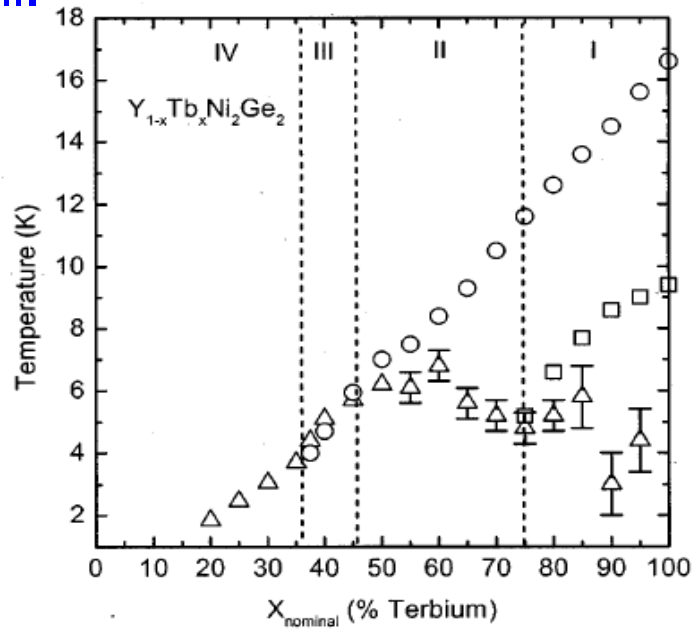


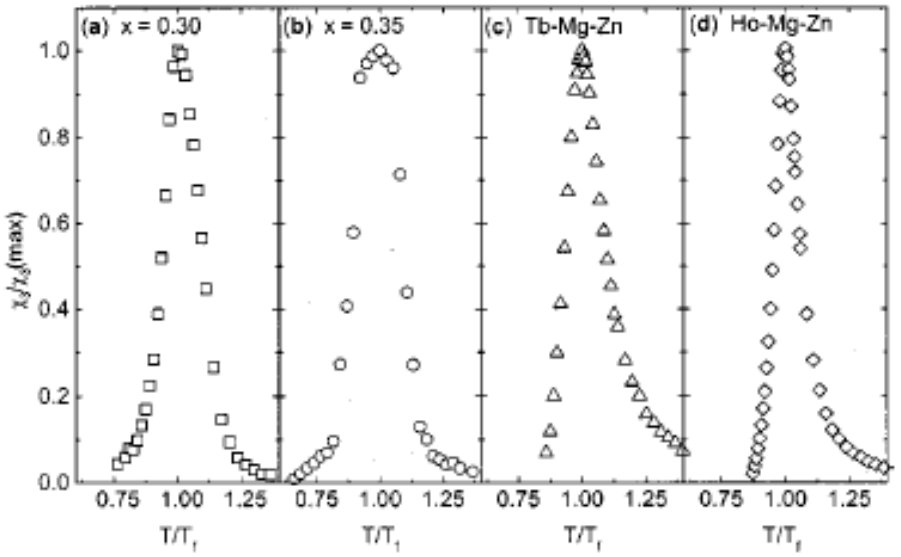
In addition to control of ordered states and field stabilized, meta-magnetic, states, the control over anisotropy that the CEF splitting offers can be used to create and study spinglass states as well.



Spinglasses part I

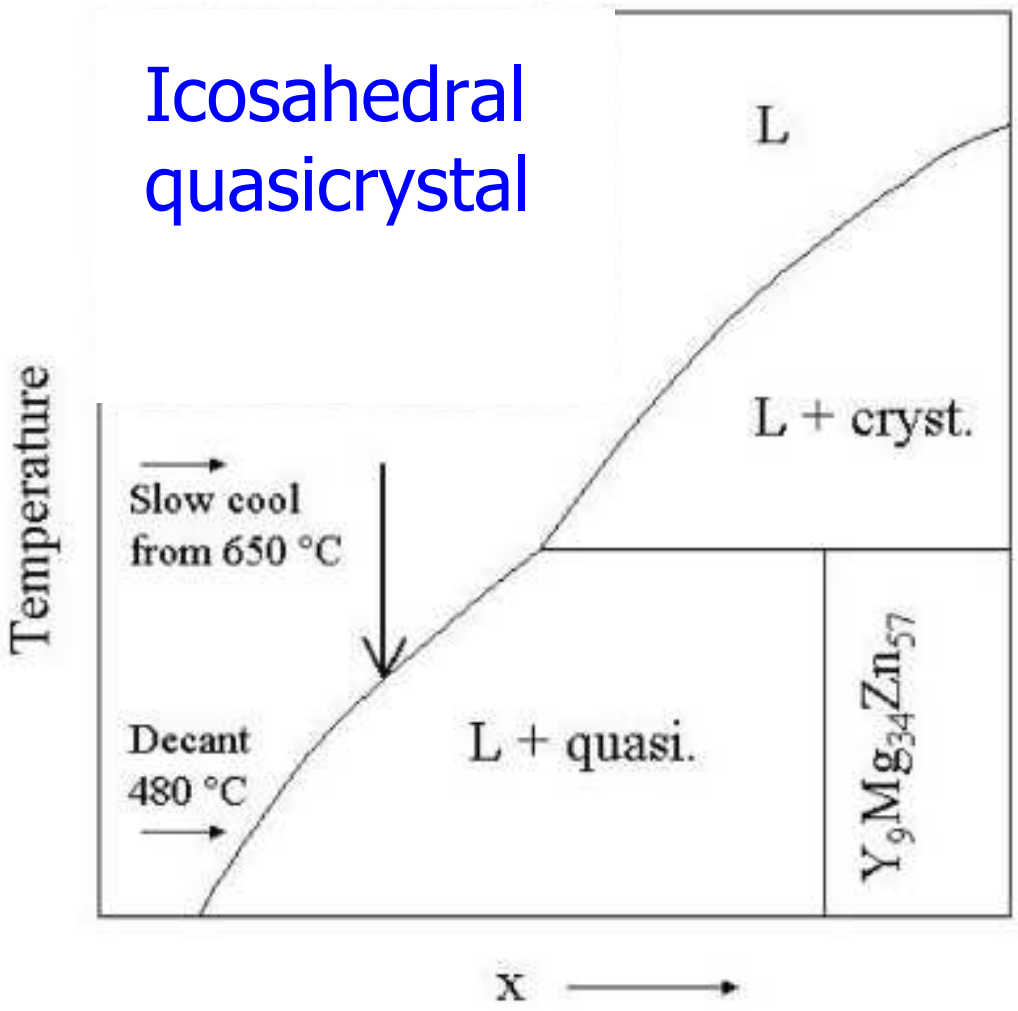
$(Y_{1-x}Tb_x)Ni_2Ge_2$ Ising spin glass system



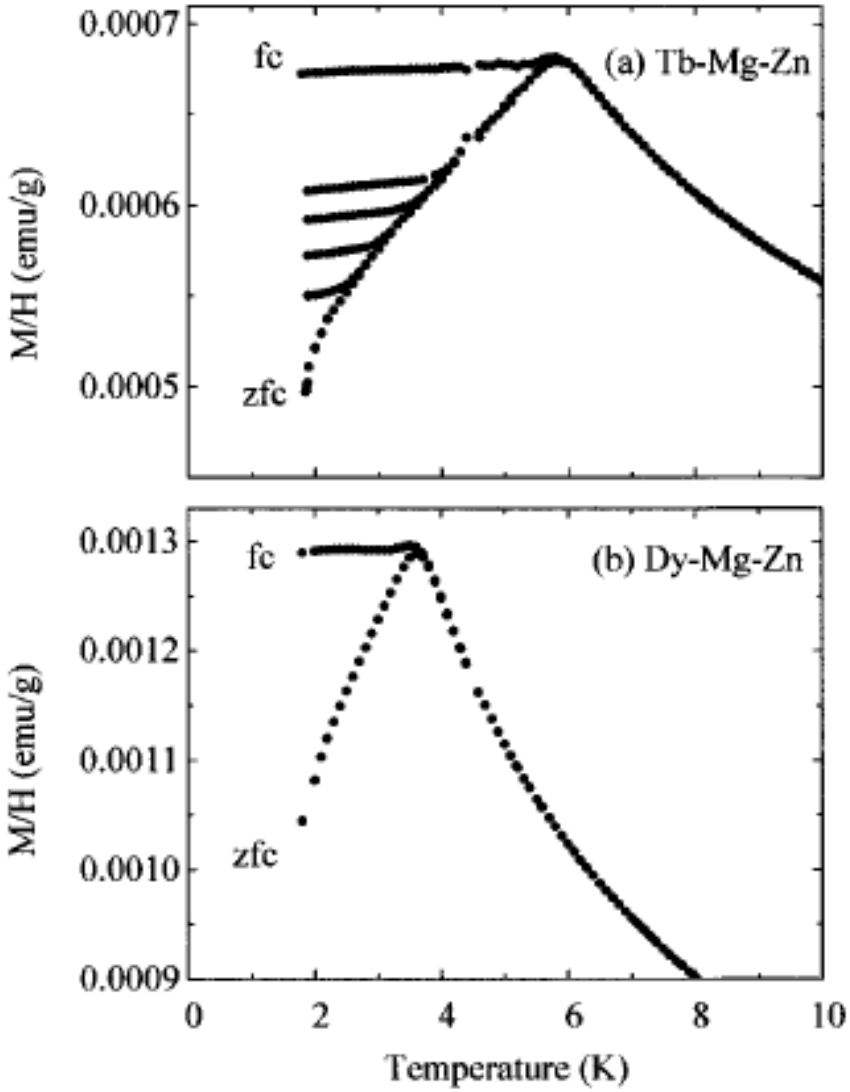


Spinglass part II: R-Mg-Zn

No long-range order, but instead an ideal spin-glass system

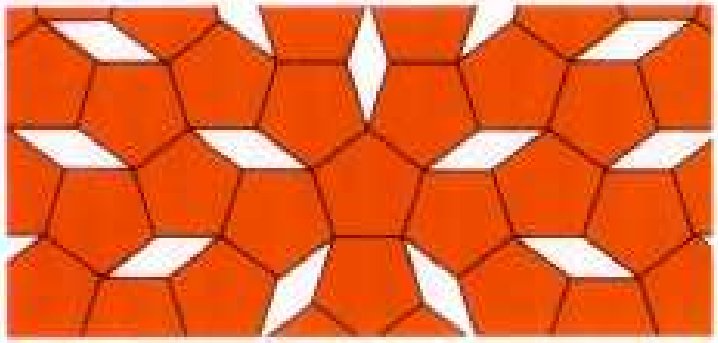


$R_xMg_{60-3x}Zn_{40-2x}$ line



We were able to grow for R = Y, Gd – Er… ***MODEL SYSTEM***

Fisher et al., PRB 59 (1999) 308, and Canfield and Fisher, J. Alloys and Comp. 317 (2001) 443

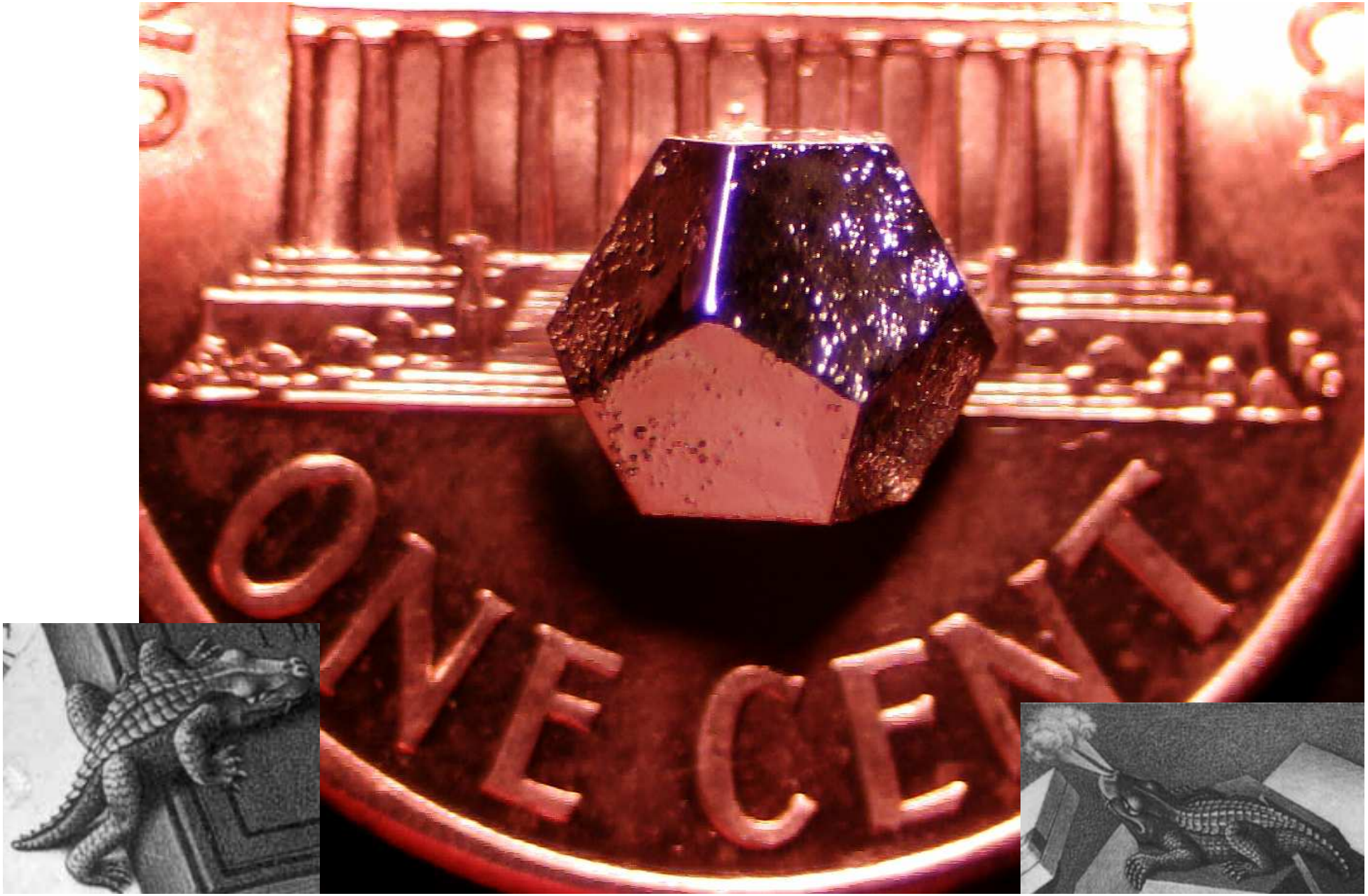


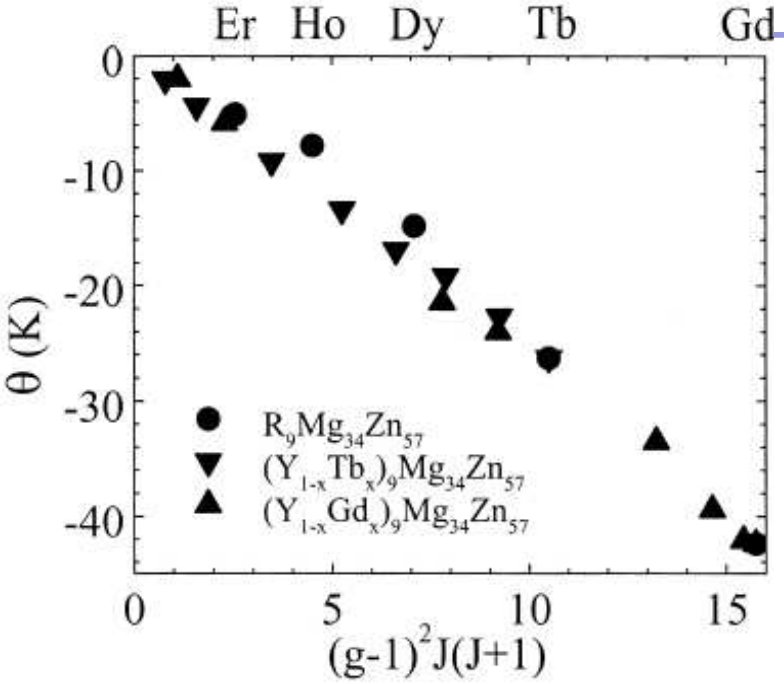
Two-dimensional crystal lattices cannot possess five-fold symmetry points because it is not possible to fill a plane completely with a network of regular pentagons (left).

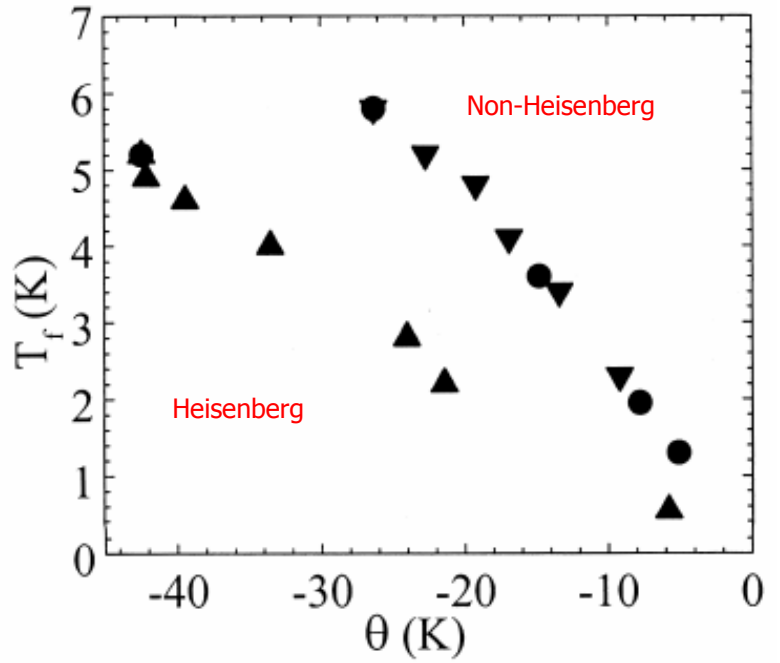
M. C. Escher gives a tip of the pen to this in his famous work: reptiles. Whereas you cannot have a tessellation of pentagons, you can form a Platonic solid: the pentagonal dodecahedron. This is what the lizard is rising out of the page and blowing smoke on….

Keep your eye on the dodecahedron….

Research Science: Yesterday's impossible is today's commonplace







Model system: *is there a difference between a Heisenberg and non-Heisenberg spinglass?*

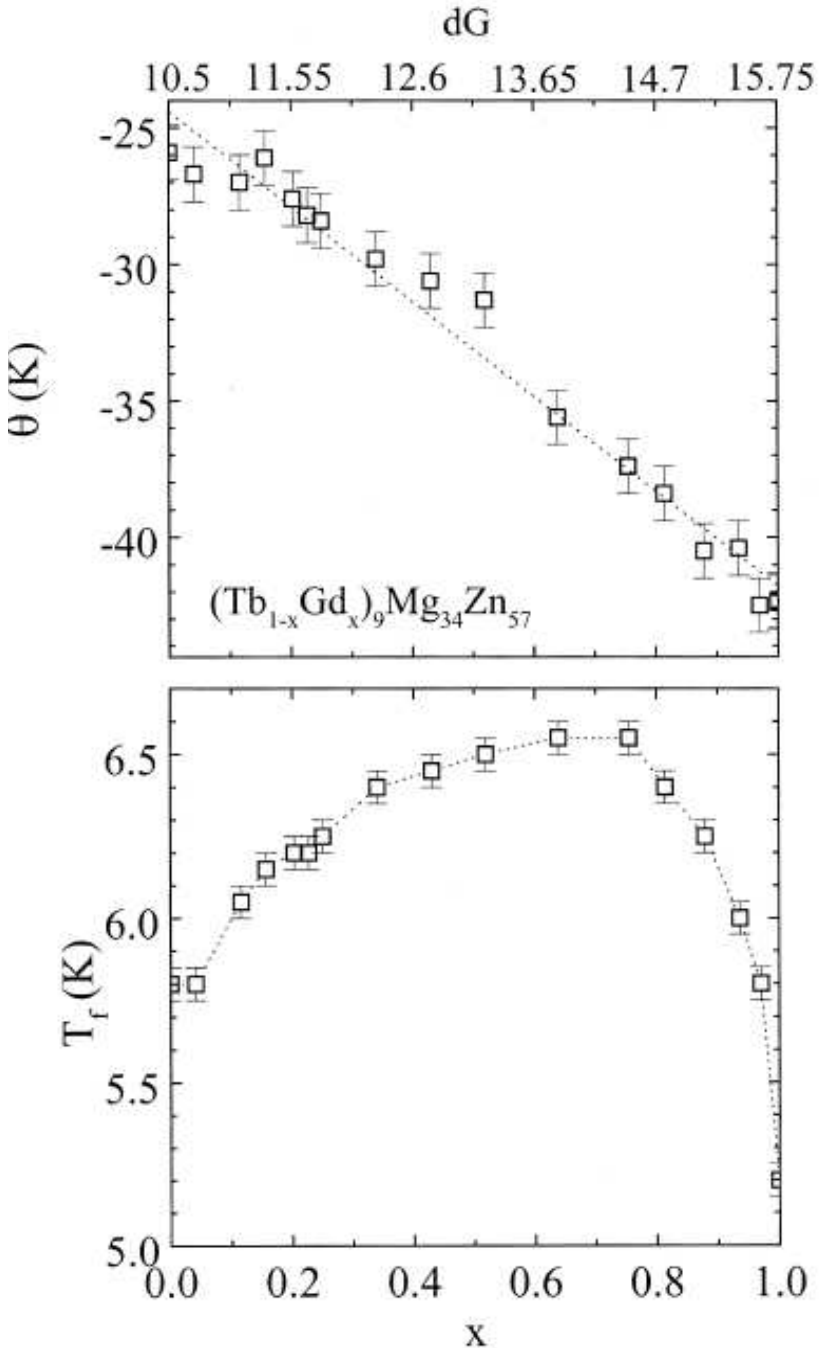
A floor covered with marbles is slippery.

If each marble is non-spherical, then the floor will be less slippery and more inclined to seize up.

A spin glass comprised of spherically symmetric moments (Gd) freezes at a lower temperature than a spin glass comprised of non-spherically symmetric moments (due to crystalline electric field splitting).

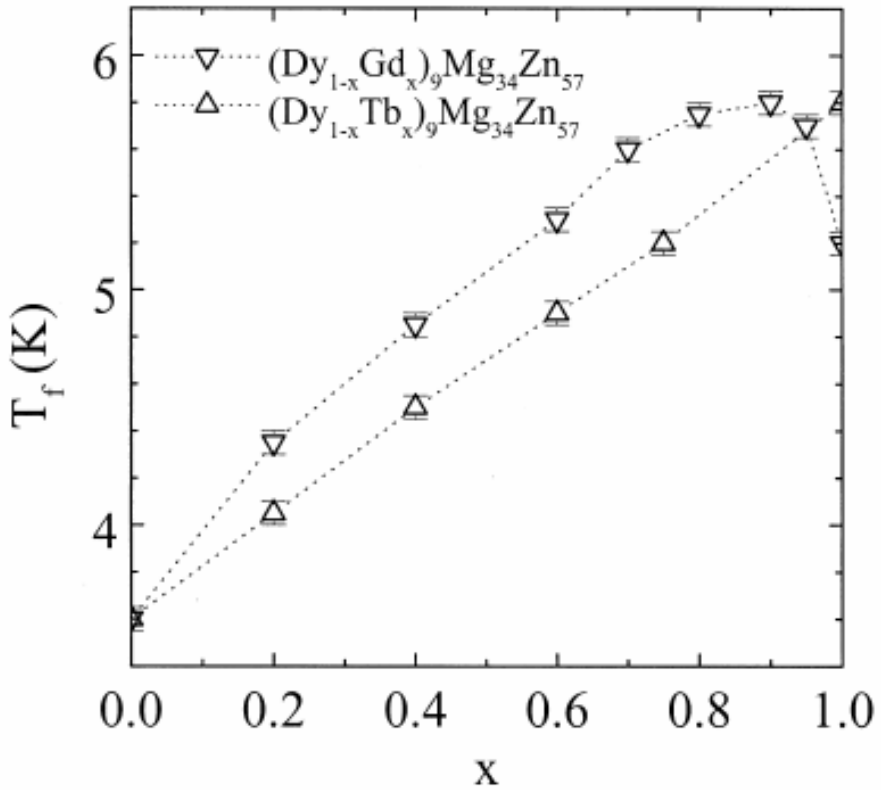
What happens if we titrate spherical moments into non-spherical moments?

Fisher et al., PRB 59 (1999) 308, and Canfield and Fisher, J. Alloys and Comp. 317 (2001) 443



As we titrate Gd into either TbMgZn or DyMgZn we see that initially T_f increases as the interaction strength increases, but beyond ~80% Gd T_f drops (beyond ~80% spheres the floor gets slippery).

This is not a disorder effect, see Dy-Tb series

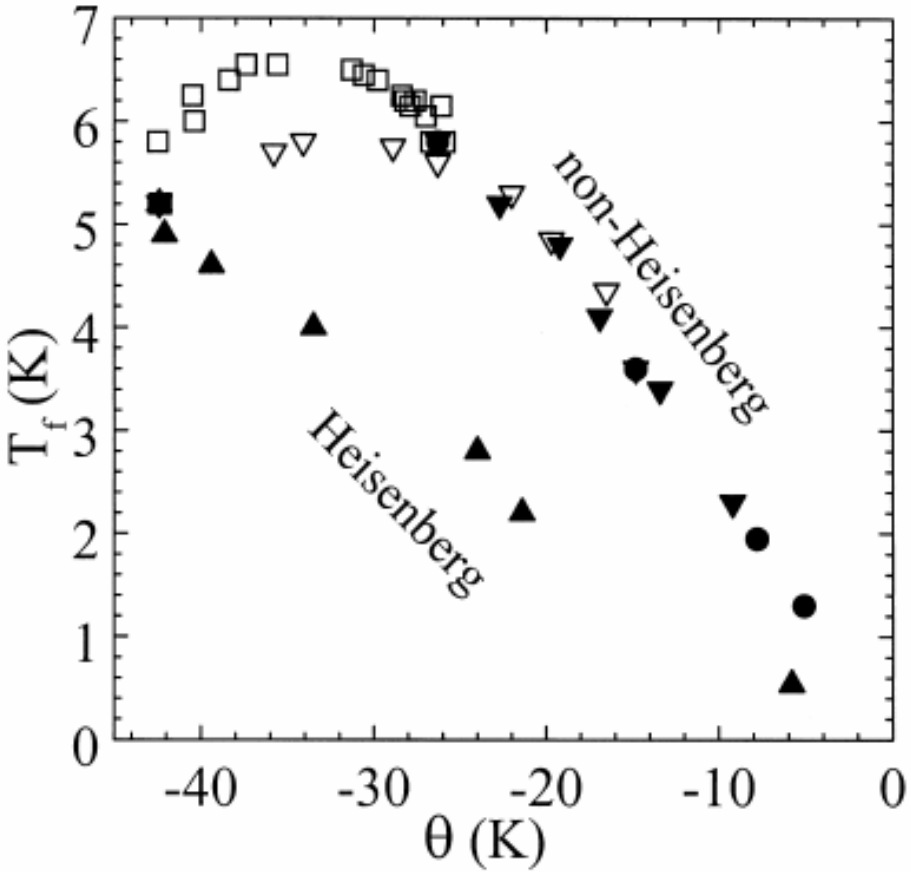


Fisher et al., PRB 59 (1999) 308, and Canfield and Fisher, J. Alloys and Comp. 317 (2001) 443

$R_9Mg_{34}Zn_{57}$ R = Y, Gd – Er Quasicrystals

For RMgZn Icosahedral quasicrystals we went from "want specific material" to "use as a model system" to examine effects of Heisenberg and non-Heisenberg moments on spin glass state manifested in an aperiodic, but highly ordered, system.

For me the RMgZn quasicrystals allowed me to replace the word, "random" with the word "aperiodic" when thinking of the spin-glass state.



Fisher et al., PRB 59 (1999) 308, and Canfield and Fisher, J. Alloys and Comp. 317 (2001) 443

A final note on CEF splitting: Kramer's Ions

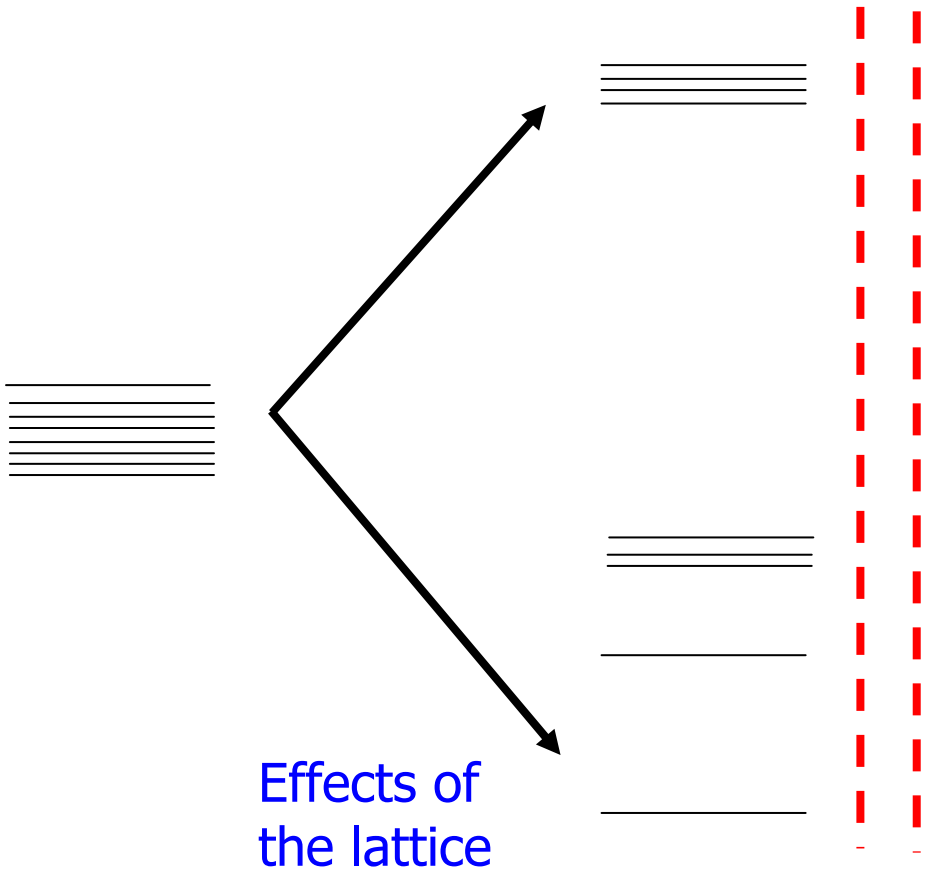
There is another systematic variation across the rare earth series, show in color below.

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb

For Kramer's ions (Ce, Nd, Sm, Gd, Dy, Er, Yb) there is a minimum degeneracy of 2 for the H = 0 CEF ground state. This means that there will be a guaranteed local moment at low temperatures and, at least, Rln2 worth of entropy that has to be removed at low temperature.

For non-Kramer's ions (Pr, Pm, Eu, Tb, Ho, Tm) there can be CEF singlet ground states. If there is a singlet there no local moment magnetization, since there is no Zeeman splitting and there is Rln1 (i.e. zero) entropy to remove…..

When the CEF split ground state is a singlet, the compound loses its local moment nature and instead manifests a van Vleck paramagnetism associated with the splitting to the first excited state.



Effects of the lattice on the rare earth

Bandstructure and coupling terms….

Non-magnetic, singlet, ground state.

T_N is much less than CEF splitting from singlet to excited state

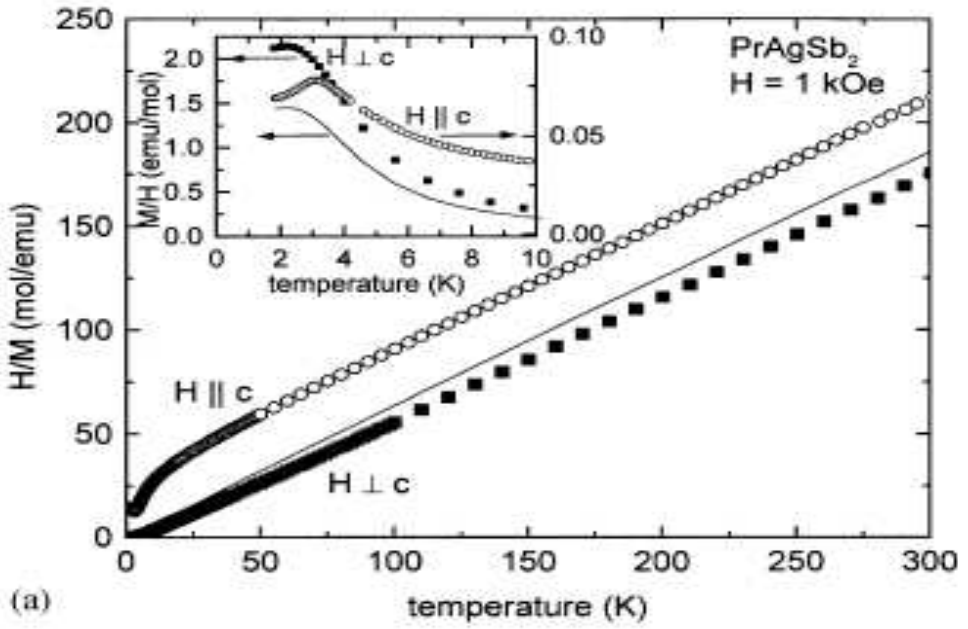
T_N

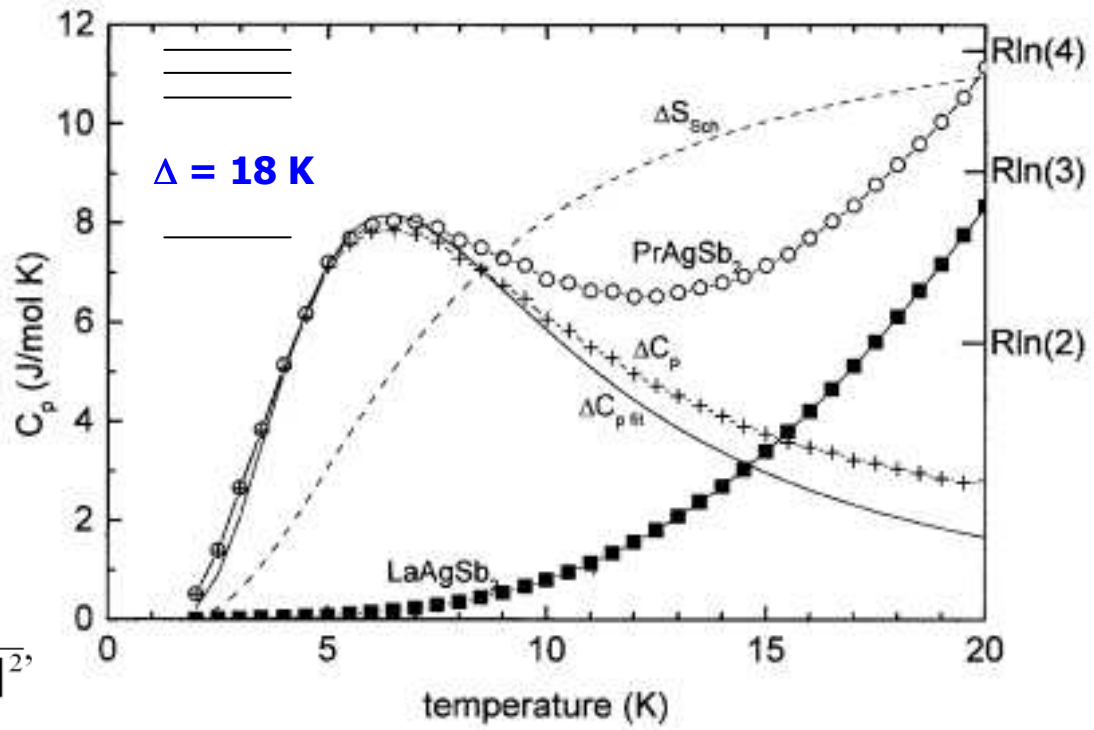
Note, this has to be an non-Kramer's ion

An experimental manifestation of this is $PrAgSb_2$, which instead of ordering at low temperatures, drops into a non-magnetic state associated with a singlet CEF split groundstate.

This can be seen in the C_p as a Schottky anomaly. This is clearly shown at the right in $PrAgSb_2$. This is modeled as a two level system.

$$C_{\mathrm{Sch}} = R\left(\frac{\Delta}{T}\right)^2 \frac{g_0}{g_1} \frac{\exp(\Delta/T)}{[1+(g_0/g_1)\exp(\Delta/T)]^2},$$





K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52

By using the rare earths, the physicist can tune the:

Size of the unit cell,

Size of the local moment and degree of coupling,

Size and direction of anisotropy,

Amount of entropy that can be removed at low temperatures,

Band filling,

Degree of hybridiztion.

In terms of temperature and energy scales (another obsession of the physicist), the rare earths can be used to tune:

The magnetic ordering temperature T_C or T_N

The CEF splitting or $T_{\Delta CEF}$

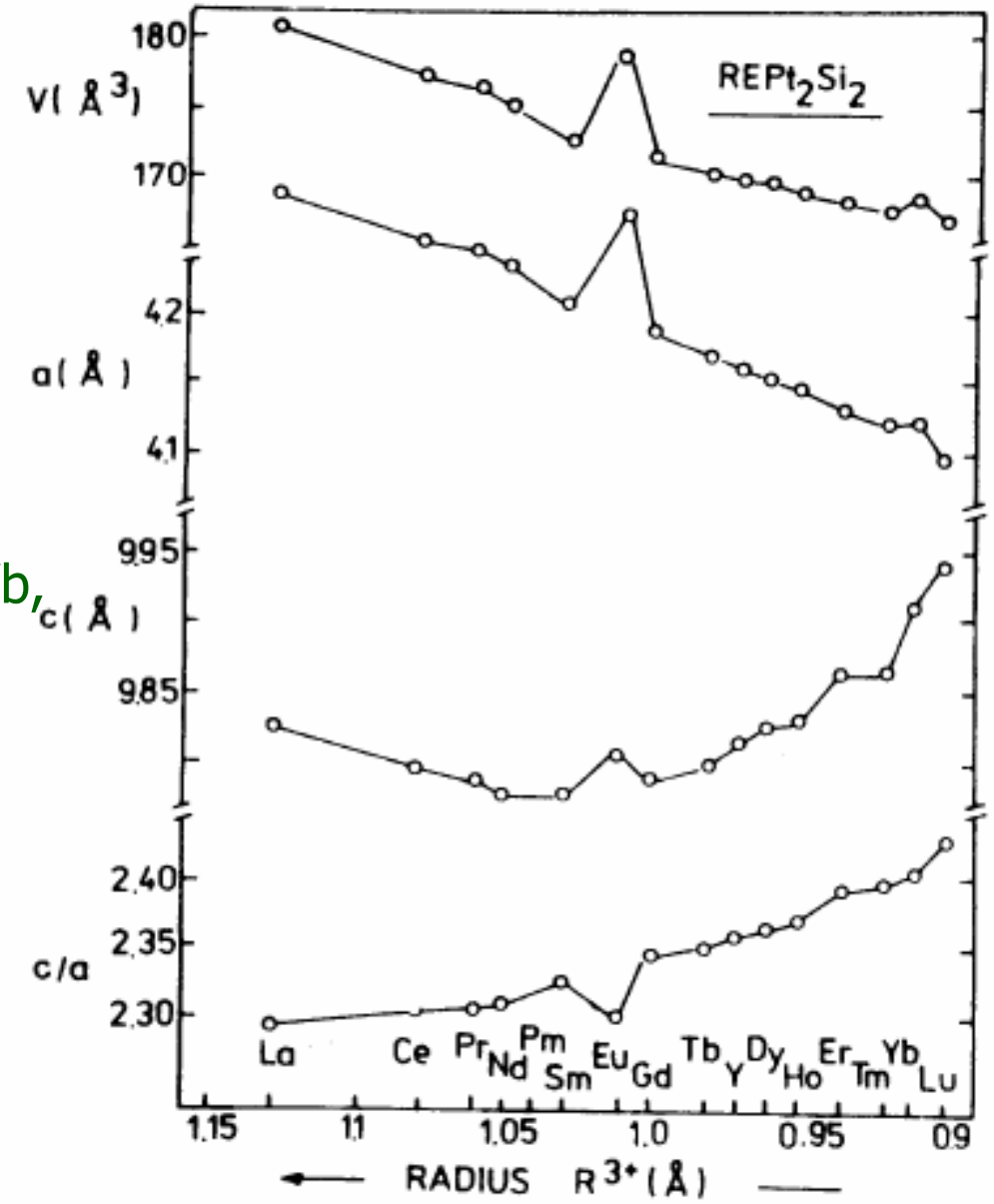
The Kondo temperature T_K

In the most extreme cases Ce^{4+}, Eu^{2+} and Yb^{2+} can be stabilized.

The empty (Ce^{4+}) and fully filled (Yb^{2+}) as well as exactly ½ filled (Eu^{2+}) 4f-shell can be more stable, leading to these deviations from the standard R^{3+} state.

This leads to non-magnetic Ce and Yb,

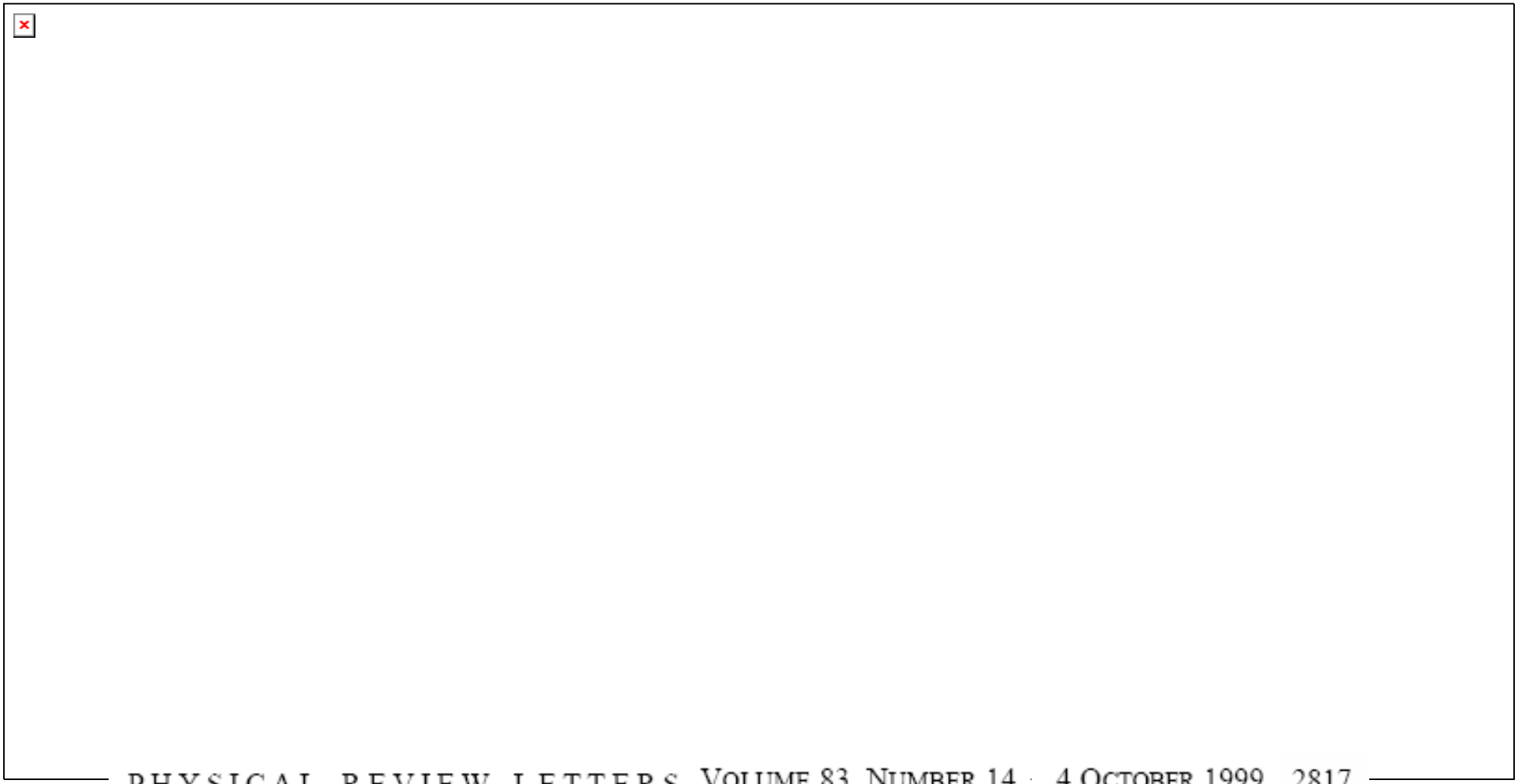
and Eu goes from non-magnetic to being the same as Gd $^{3+}$, but with different band filling.

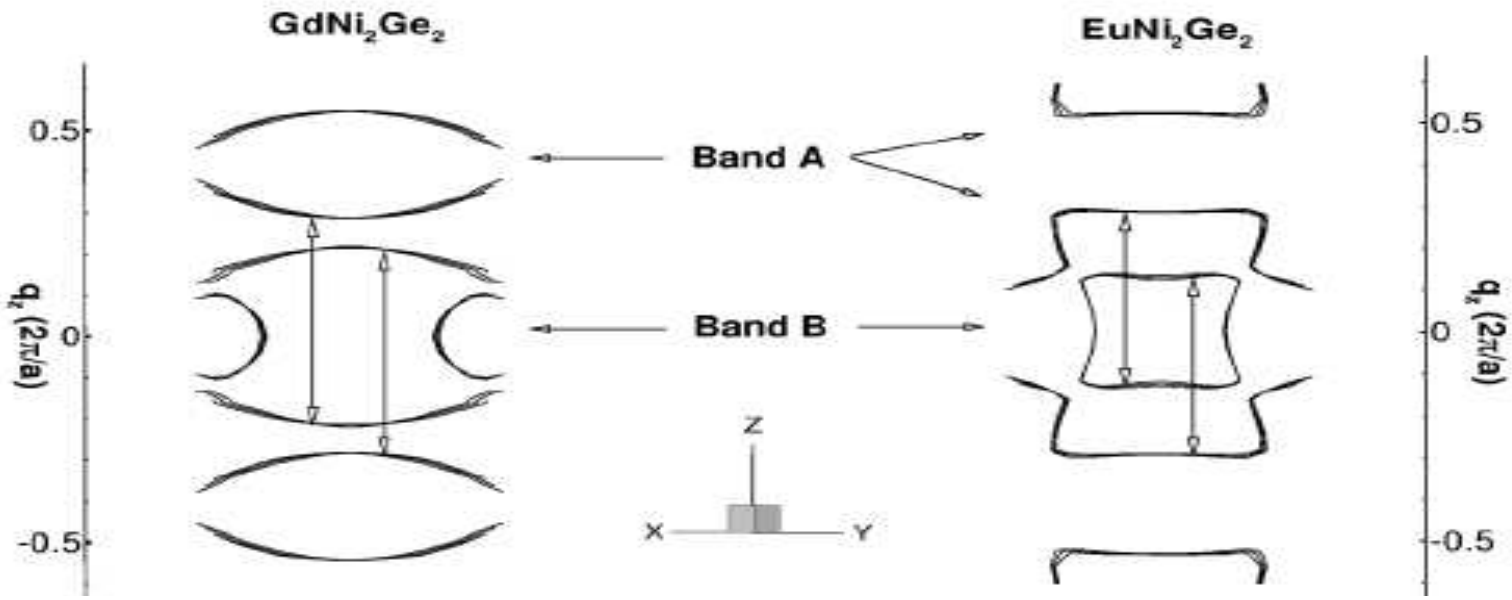


The effects of band filling on magnetism can be probed with Gd^{3+} and Eu^{2+} isostructural materials

q = (0 0 0.793 – 0.805)

q = (0 0 1)

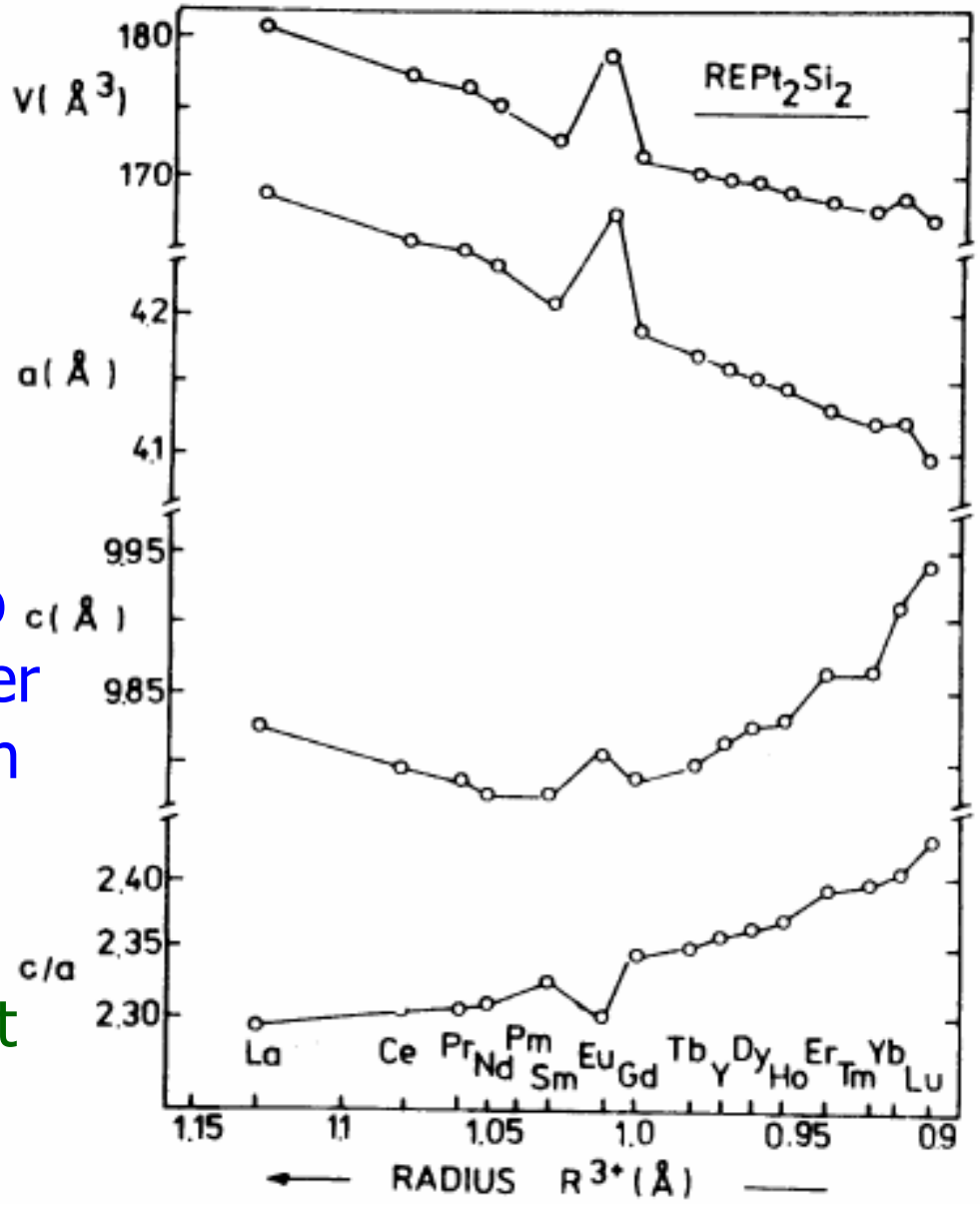



GdNi2Ge2
EuNi2Ge2
Band A
Band B
0.5
0
-0.5
qz (2π/a)
Z
X
Y

In only the most extreme cases Ce^{4+}, Eu^{2+} and Yb^{2+} can be stabilized.

But even when, Ce and Yb appear to be essentially 3^+ at room temperature, at low temperature, below a characteristic temperature, T_K, they can hybridize with the conduction band. This leads to a loss of local moment character and strongly correlated electron effects.

This more subtle interaction is at the heart of the Kondo effect and heavy fermions.



Hybridization, heavy fermions, and entropy

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb

For Kramer's ions (Ce, Nd, Sm, Gd, Dy, Er, Yb) there is a minimum degeneracy of 2 for the H = 0 CEF ground state. This means that there will be at least Rln2 worth of entropy that has to be removed by (i) magnetic ordering or ***(ii) some other, more exotic, mechanism.***

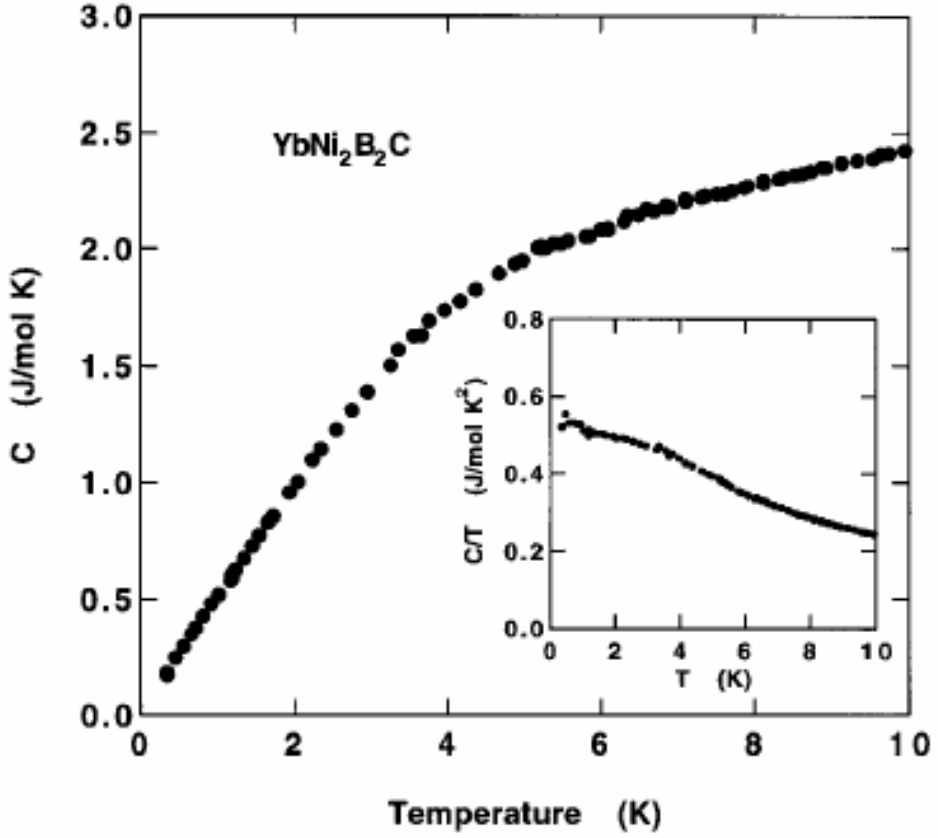
One such mechanism for R = Ce, Sm, Yb is to allow hybridization between the 4f electrons and the conduction electrons below a characteristic T_K. This leads to Kondo lattices…heavy fermions.

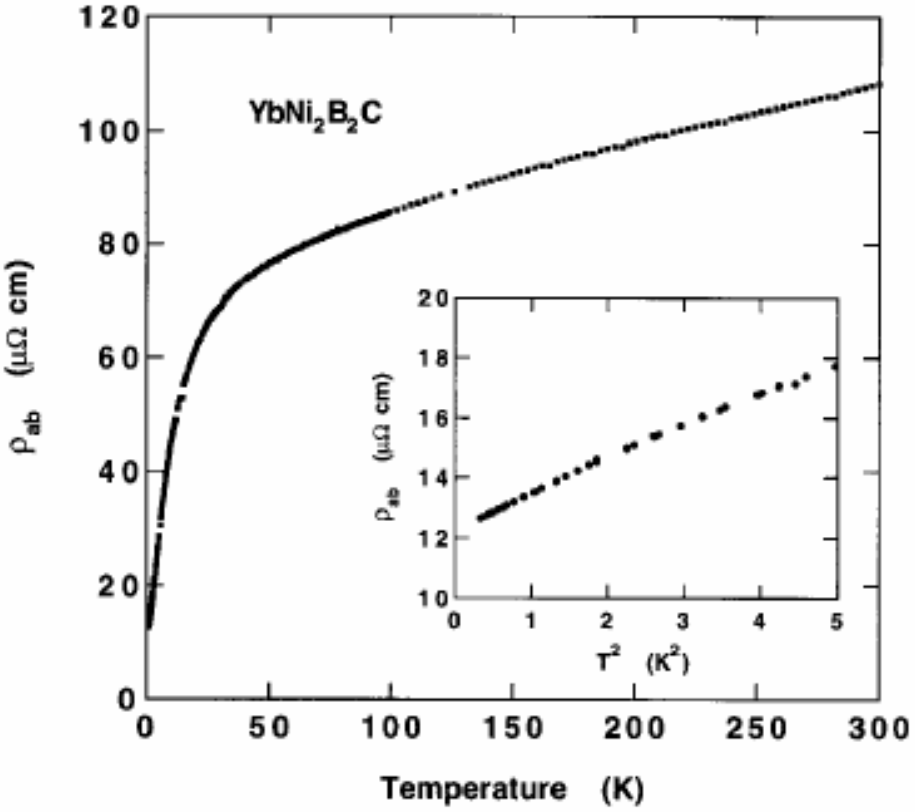
$\gamma T_K \sim$ Rln2 for a CEF doublet groundstate

γ is proportional to the electron mass. Large γ implies large m, ∴ heavy fermion.

Whereas this ground state has been extensively studied in Ce-based compounds, until recently there has been a dearth of Yb-based examples.

$YbNi_2B_2C$ – The rare, model Yb-based heavy fermion





γ=530 mJ/mol K^2

$T_N, T_c << T_K << T_{\Delta CEF}$

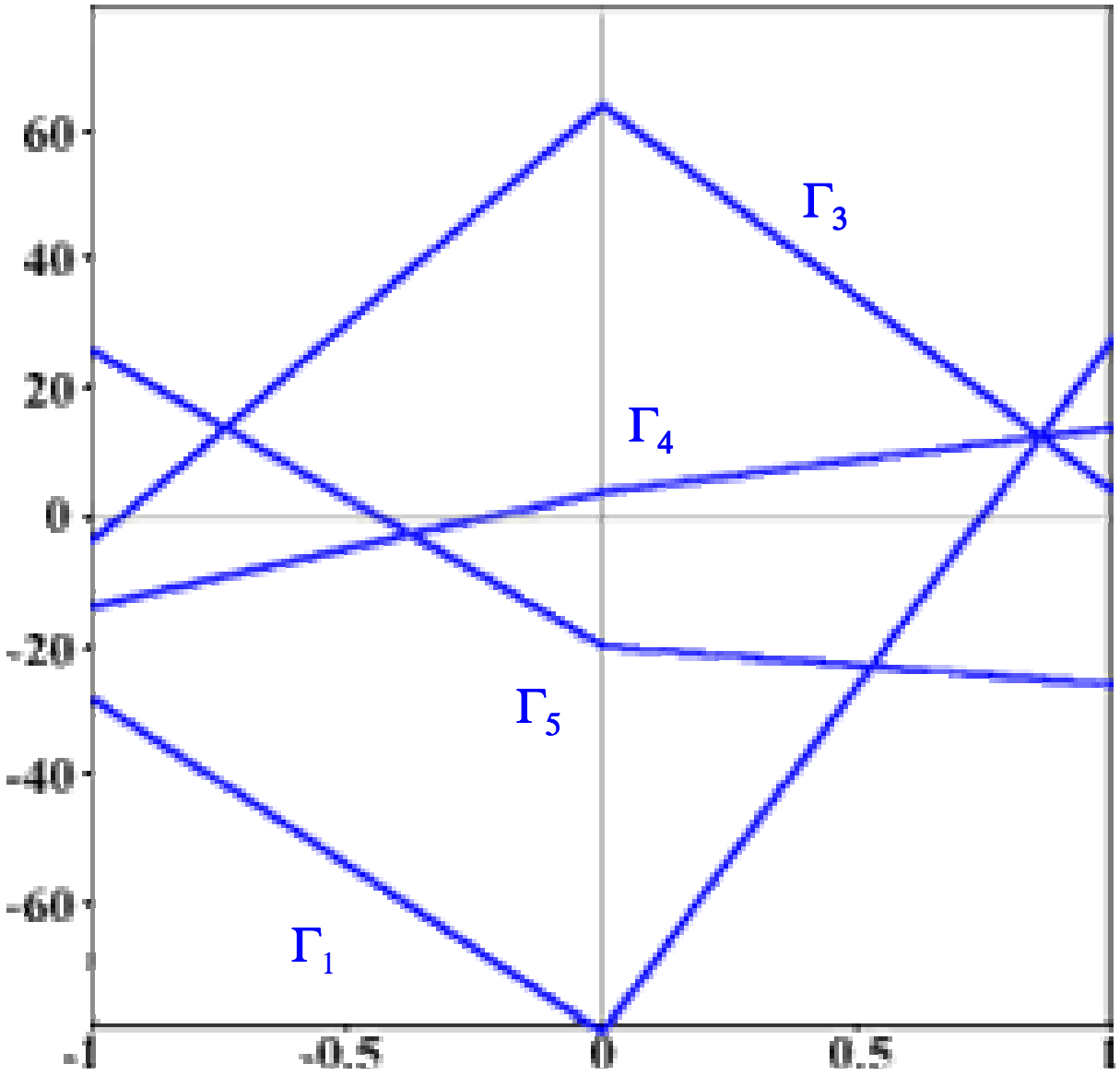
0.03 K << 10 K << 100 K

This separation of energy scales makes $YbNi_2B_2C$ a model heavy fermion system!

Yatskar et al., PRB 54 (1996) 3772

What about non-Kramers ions: Can entropy be preserved in Pr-based samples to low enough temperatures to allow for hybridization? i.e. can a Pr-based sample go heavy?

Cubic point symmetry can help preserve entropy of this non-Kramer's ion. (The Γ_3 state is a non-magnetic doublet and can, sometimes, be the ground state)



Lea, Leask, Wolf splitting for Pr^{3+}

K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

Make a list of cubic compounds with a single RE in cubic point symmetry, refine list, make compounds, hunt physics.

cF12

AcH_2 (A)
Al_2Au (B)
$AlNi_2Si_2$ (B)
Al_2Pt (A) (B)
As_3GeLi_5
As_3Li_5Ti
AsNaZn
$AsRh_2$ (A)
$AuGa_2$
$AuIn_2$ (A)
BiO_2 (B)
CaF_2
CdLiSb
ClO_2
CoMnSb
Cu_2Se (B)
ErH_2 (A)
$Fe_2Ni_7Si_{10}$ (B)
GdH_2Y (A) (B)
$GeMg_2$
H_2La (B) (A)
H_2Nb
H_2Np (B) (A)
H_2Sc
H_4TaV (B)
H_4TiV (B)
H_2Y (A)
HfO_2
IrMnSb
K_2S
LiMgN
Li_2O
Li_5P_3Ti
Li_2S
Mg_2Pb
Mg_2Si (A)
Mg_2Sn
Na_2S
$NiSi_2$ (A)
O_2Pb
O_2Pu
O_2Tb (A)
O_2U
PRh_2
Rb_2Se

cF16

Ag_2AlSc
$AgCd_2Ce$
Ag_2CeIn
Ag_2ErIn
AgAsZn
Al_7Cu_4Li
Al_2Pd (A)
AmH_2 (B)
As_4Li_7Mn
As_4Li_7V
$As_2P_3Rh_{10}$ (B)
Au_2CdIn_2Sn (B)
$Au_{17}Ga_{30}Pd_3$ (B)
BBe_2 (A)
BkH_2
$CdLi_2MgP_2$ (B)
CeH_2 (B) (A)
CmH_2 (A)
$CoNiSi_4$ (B)
DyH_2 (A)
$ErH_{20}Y_9$ (A) (B)
Ga_2Pt
Gd_2O_3
H_2Hf
H_2Lu (A)
H_4NbV (B)
H_2Pr (B)
H_2Sm (B)
H_2Tb
H_2Tm (A)
H_2Yb (A)
Ho_2O_3
Ir_2P
K_2Se
LiMgP
Li_2P_2Si
Li_7P_4V
Li_2Se (B)
$Mg_5Sb_2Si_2$ (B)
Mg_7SiSn_2 (B)
MnPtSn
Na_2Se
NpO_2 (A)
O_2Po
ORb_2 (A)
O_3Tb_2
OZr
$PtSn_2$
$AgAuCd_2$
Ag_2CdMg (B)
$AgCeMg_2$ (B)
$Ag_{12}GaMg_5$ (B)

Structure Type CaF_2 — Space Group $Fm\bar{3}m$ — No. 225

$AgCuTe$
$AlIrMn$
$Al_{13}Pd_4Si_3$ (B)
AmO_2
As_2Li_2Si
$AsLiZn$
As_4PRh_{10} (B)
$AuCdSn$
$Au_{19}Ga_{46}Pd$ (B)
Be_2C
BkO_2
$CdLi_2P_2Zn$ (B)
CeO_2 (B)
CmO_2 (B)
$CoSi_2$
Dy_2O_3
Er_2O_3
GdH_2 (A)
$GeLi_2P_2$
H_2Ho
H_4Mg_2Ni (F)
H_2Nd (B) (A)
H_2Pu (B)
H_2Ta
H_2Ti (A) (B)
H_2V (A) (B)
H_2Zr (A) (B)
In_2Pt
K_2O
K_2Te
Li_7MnP_4
Li_2P_2Sn
LiPZn
Li_2Te
Mg_5Sb_2Sn (B)
Mg_7Si_2Sn (B)
N_2U (A)
Na_2Te (A)
O_2Pa
O_2Pr (B)
O_3Sm_2 (A)
O_2Th
O_2Zr (A)
Rb_2S

Structure Type BiF_3 — Space Group $Fm\bar{3}m$ — No. 225

$AgAuZn_2$ (B)
$AgCeCsIn$ (B)
Ag_2DyIn
Ag_2GdIn
$AgGdMg_2$ (B)
Ag_5InMg_4 (B)
Ag_2InPr
Ag_2InTb
Ag_2LaMg (B)
Ag_2LiSn
$AgMg_2Sm$ (B)
$AlAu_2Hf$
$AlAu_2Ti$
$AlCo_2Fe$
$AlCo_2Nb$
$AlCo_2V$
$AlCrFe_2$
$AlCu_2Mn$
$AlCu_2Sc$
$AlFe_2$

cF16

Ag_2HoIn
$Ag_4In_3Mn_5Pd_8$ (B)
Ag_2InSc
Ag_2InTm
$AgLi_2Mg$
$AgMg_2Nd$ (B)
$AgMg_2Tb_2$ (B)
$AlAu_2Mn$
$AlBiPd_2$ (A)
$AlCo_2Hf$
$AlCo_2Ta$
$AlCo_2Zr$ (B)
$AlCrNi_2$
$Al_6Cu_6Mn_5Pd_4$ (B)
$AlCu_2Ti$
$AlFeMn$ (B)
$AlFe_2Ni$
$AlFe_2V$ (B)
$AlHfPd_2$
$AlMnPd_2$
$AlMn_2V$
$AlNi_2Ta$
$AlNi_2Zr$
$As_3Bi_2Pd_{15}$ (A)
Ag_2InLa
Ag_2InNd
Ag_2InSm
Ag_2InY
$AgLi_2Sn$ (A)
$AgMg_2Pr$ (B)
Ag_2MgZn (B)
$AlAu_2Sc$
$AlCo_2Cr$
$AlCo_2Mn$
$AlCo_2Ti$ (B)
$AlCrCu_2$
$AlCu_2Hf$
$Al_{17}Cu_{40}Mn_{20}Sn_3$ (B)
$AlCu_2Zr$
$AlFe_2Mn$
$AlFe_4Si$ (B)
$AlHfNi_2$
$AlIr_2Mn$
$AlMnPt_2$
$AlNbNi_2$
$AlNi_2Ti$ (A) (B)
$AlPd_2Sc$
As_4InPd_{15} (A)

Structure Type BiF_3 — Space Group $Fm\bar{3}m$ — No. 225

Au_2InY
$AuLi_2$
Au_2SnU
$BeNi_2Si$
$BiGePd_2$ (A)
$BiLi_2Mg$
$BiPd_2Y$
Ca_2Tl
$CdGeLi_2$ (A)
$CdLi_2Sn$ (A)
$CeCuMg_2$ (B)
$CeMg_2$
$Co_{10}CrMn_4Si_2$
$CoFe_2Ga$
Co_2FeGe
Co_2FeSi (B)
$CoGa_2Mn$ (B)
Co_2GaTa
Co_2GeLi
Co_2GeTi
$CoMnNiSn$ (B)
CoMnSb

$AgCdMg_2$ (B)
Ag_5InMg_4 (B)
Ag_2InPr
Ag_2InTb
Ag_2LaMg (B)
Ag_2LiSn

One of many pages from Pearson's Handbook of crystallographic data….

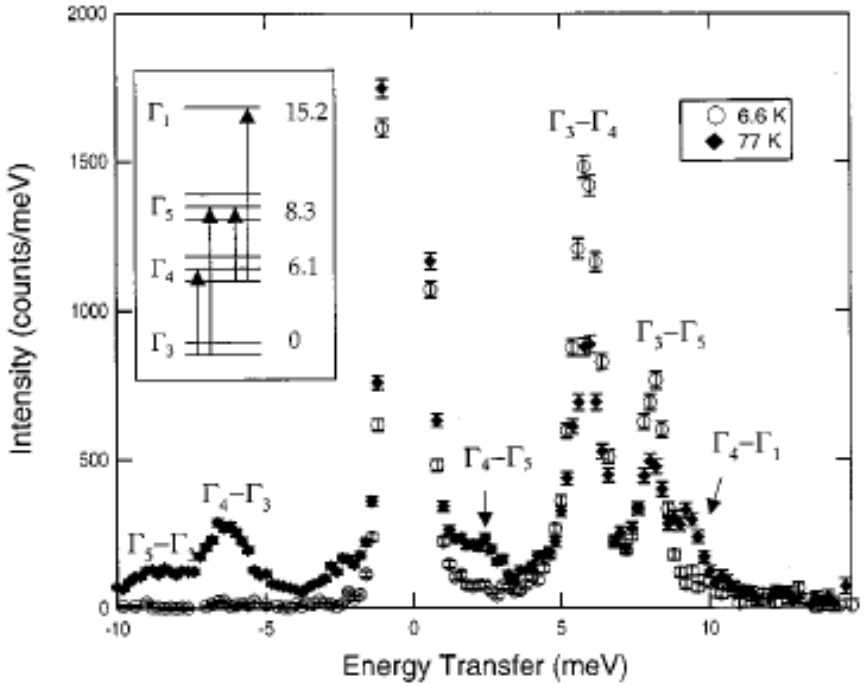
$PrAg_2In$ matched the cascade of requirements:

Cubic unit cell

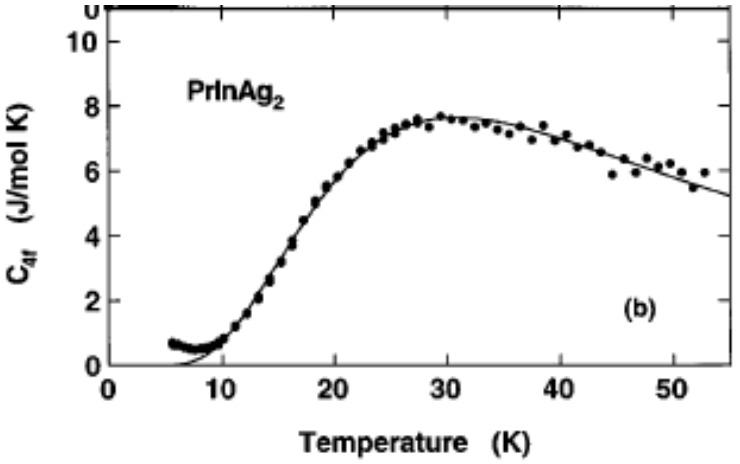
Cubic point symmetry for Pr

Γ_3 CEF groundstate

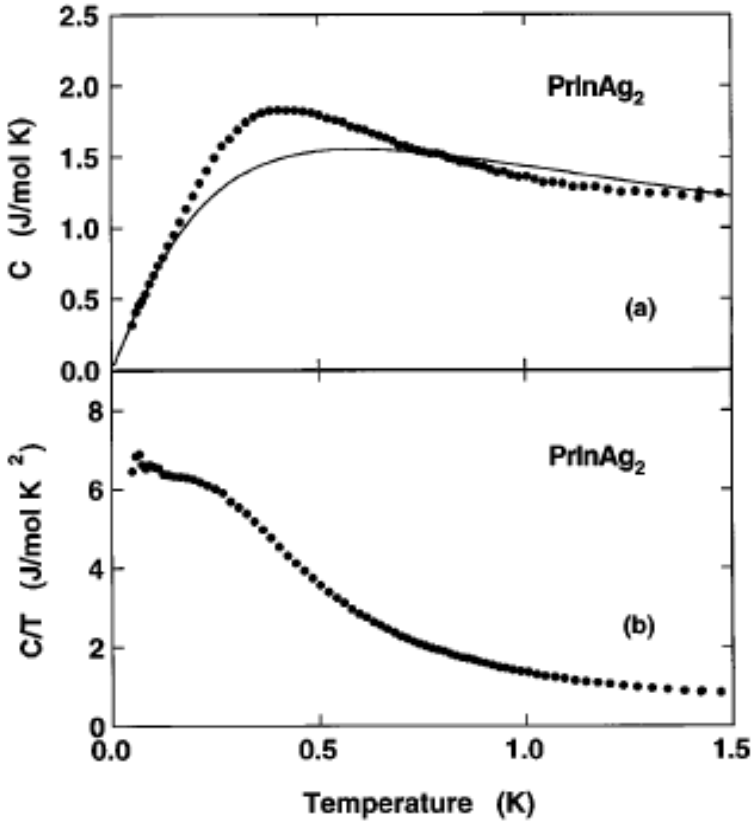
Large C/T for T < 300 mK



Kelly et al., PRB 61 (2000) 1831



Yatskar et al., PRL 77 (1996) 3637



$PrAg_2In$

Can entropy be preserved in Pr-based samples to low enough temperatures to allow for hybridization?
Yes, if done carefully….cubic unit cell, cubic point symmetry.

Can a Pr-based sample go heavy?
Yes, but it is fundamentally different physics since the heavy fermion ground state is evolving from a non-magnetic CEF level. My pet theory is dynamic screening of Jahn-Teller distortion as mechanism for entropy transfer….

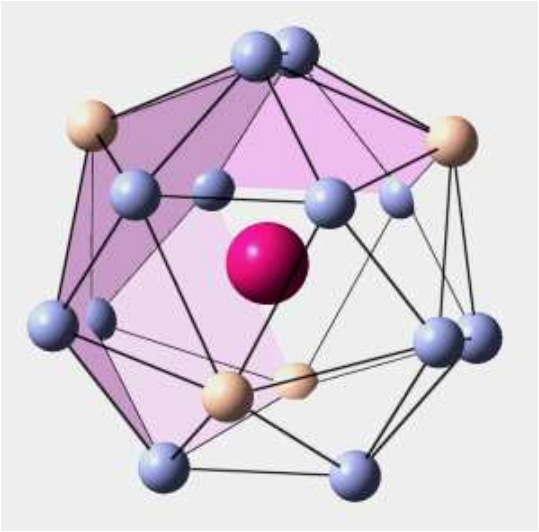
$PrAg_2In$ opened the area of Pr-based heavy fermion research and generalized the idea of preservation of entropy as a route to heavy fermion ground states. This system inspired several searches for other examples.

Recently this dearth of Yb-based heavy fermions has been ameliorated

YbT_2Zn_{20}

--Hybridizing members of the RT_2Zn_{20} series are examples of ordered Kondo lattices that are approaching a single ion impurity concentration level.

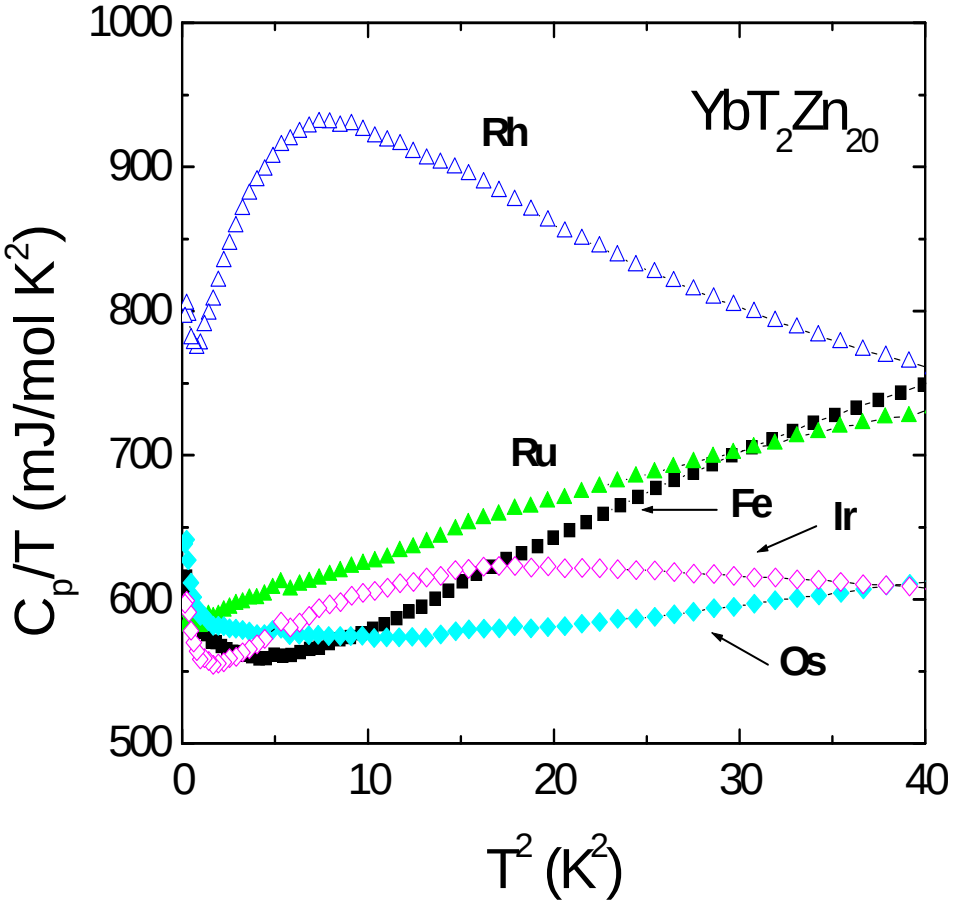
--For T = Fe, Co, Ru, Rh, Os, Ir we have discovered ***SIX NEW*** Yb-based heavy fermion compounds. *(Formally, doubling the number of such compounds!)*

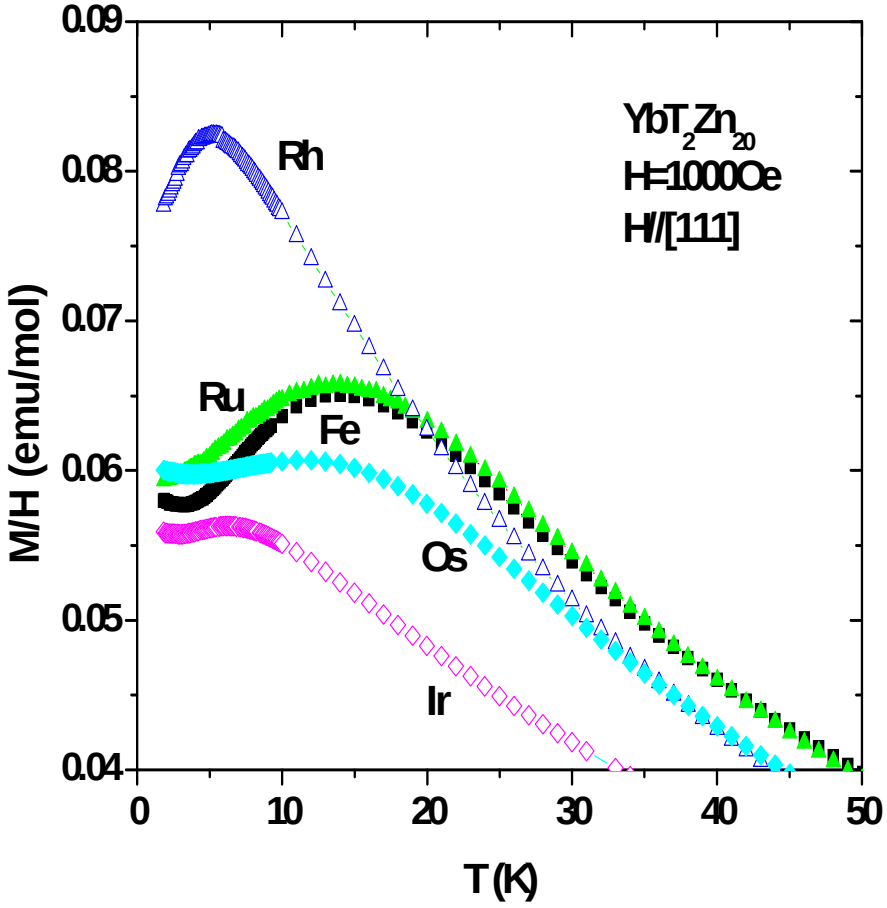


With very similar R coordination, this half dozen new systems allows for comparison of the thermodynamic and transport properties between very closely related heavy fermion compounds.

Torikachvili, et al. Proceedings of the National Academy of Sciences of the United States of America (2007), 104(24), 9960-9963.

For T = Fe, Ru, Rh, Os & Ir, clear loss of local moment behavior at low T

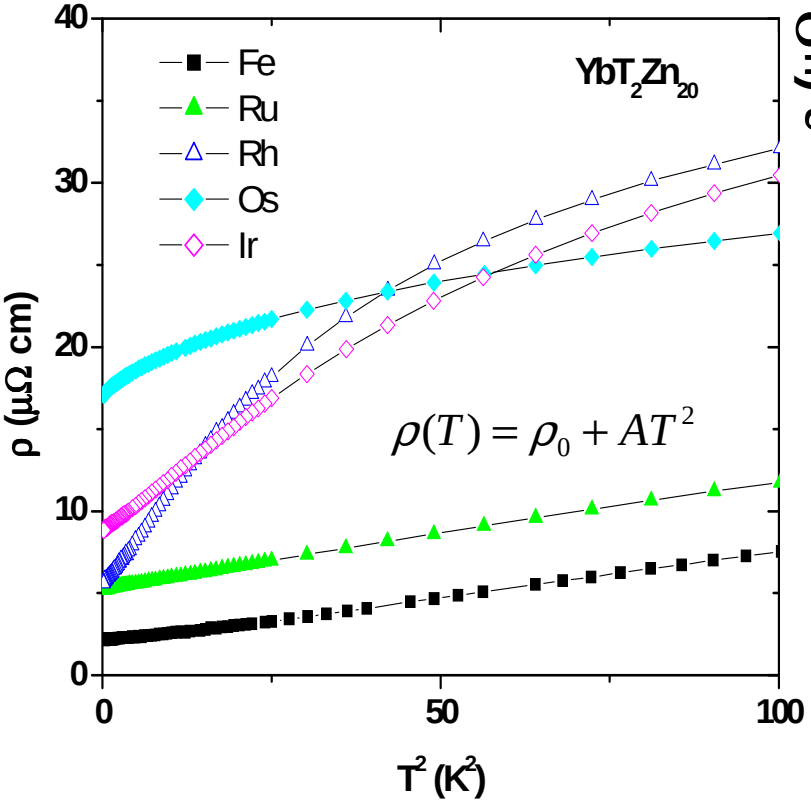


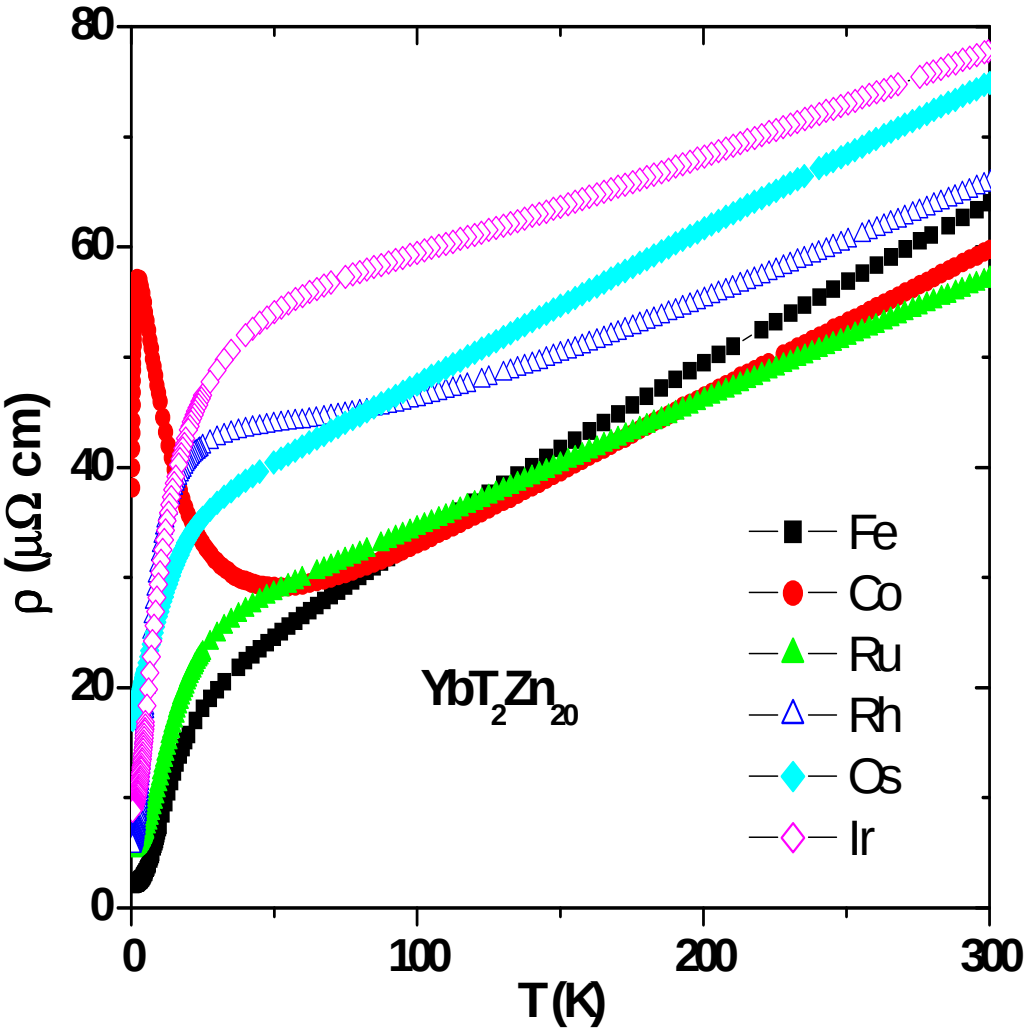


The compounds appear to be an example of a Yb-based heavy fermion with large γ.

Torikachvili, et al. Proceedings of the National Academy of Sciences of the United States of America (2007), 104(24), 9960-9963.

T-dependent resistivity of these 6 compounds manifest classic heavy fermion features; 5 *very* similar and $YbCo_2Zn_{20}$ related.





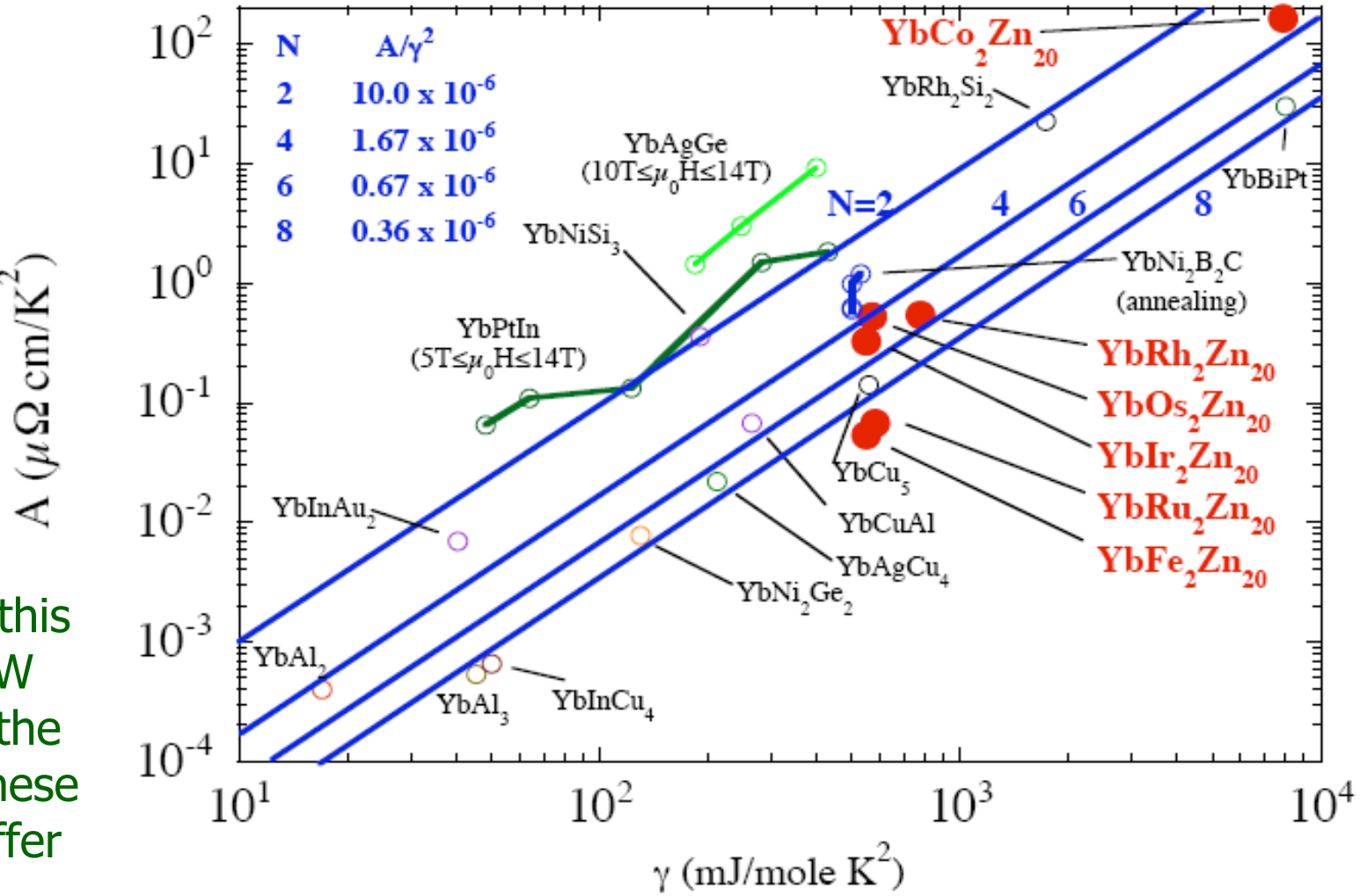
These 5 compounds show clear T^2 dependencies at low T.

Torikachvili, et al. Proceedings of the National Academy of Sciences of the United States of America (2007), 104(24), 9960-9963.

We can plot the data for our six new YbT_2Zn_{20} heavy fermions on a Kadowaki-Woods plot with some other Yb-based systems. We see that for T = Fe, Ru, Rh, Os, Ir there is a vertical spread that implies a significant difference in the Yb ion degeneracy for $T \sim T_K$. E.g. for T = Fe, Ru have higher $T_K / T_{\Delta CEF}$ ratios.

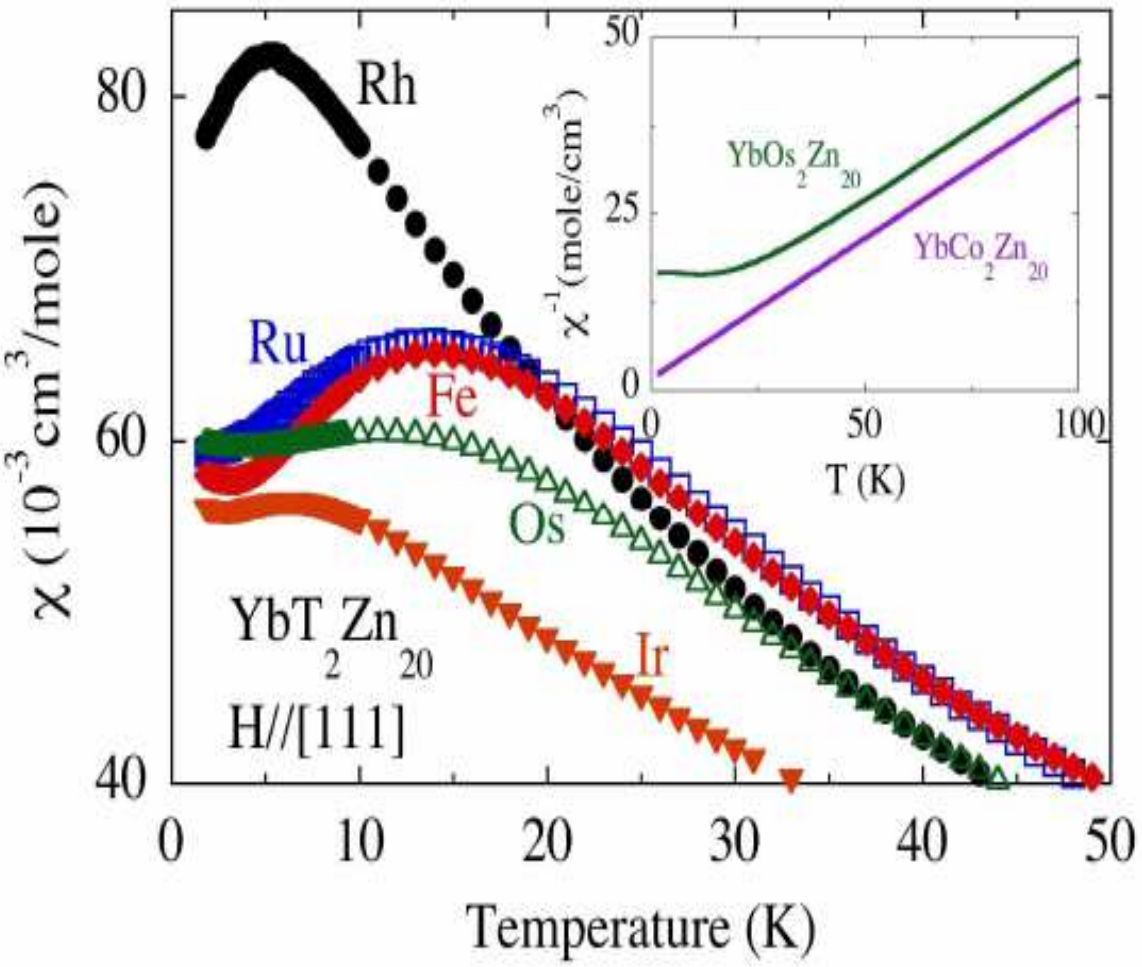
Can we correlate this with other data we have collected?

Can we gain some faith in this generalized KW plot by using the systematics these compounds offer us?



At a qualitative level:

--The temperature of χ_{max} can be used as a caliper of the Kondo temperature. For T = Ru and Fe χ_{max} occurs near 14 K and for T = Ir and Rh χ_{max} occurs near 6 K. (T = Os is intermediate.)

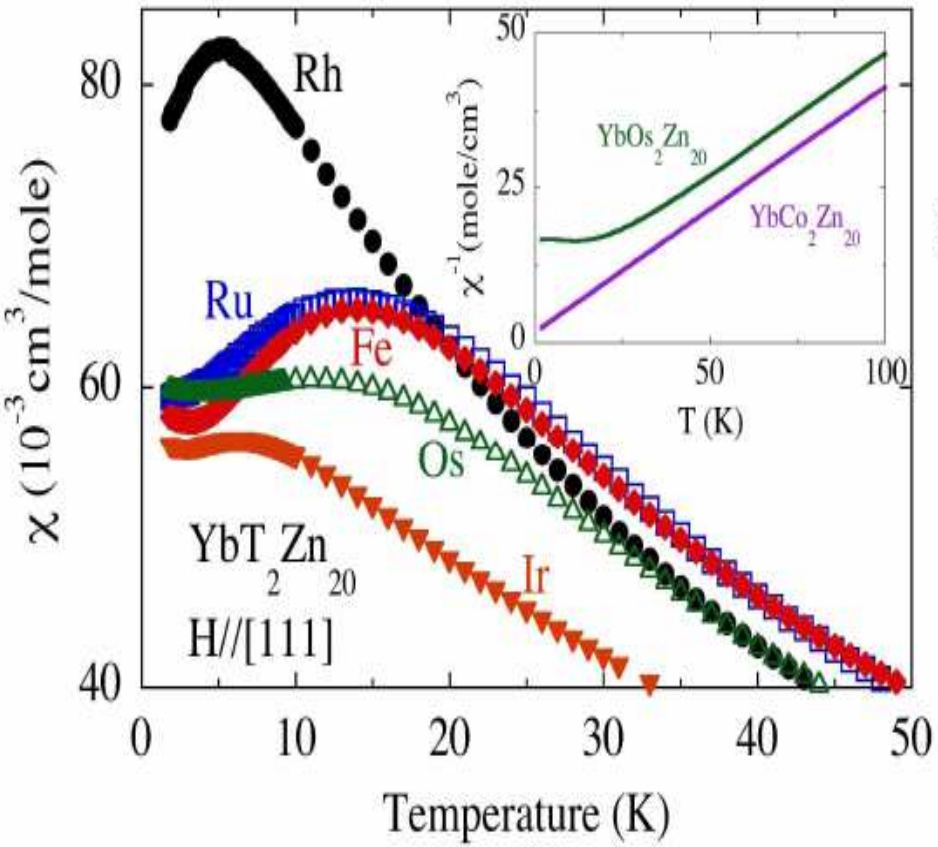


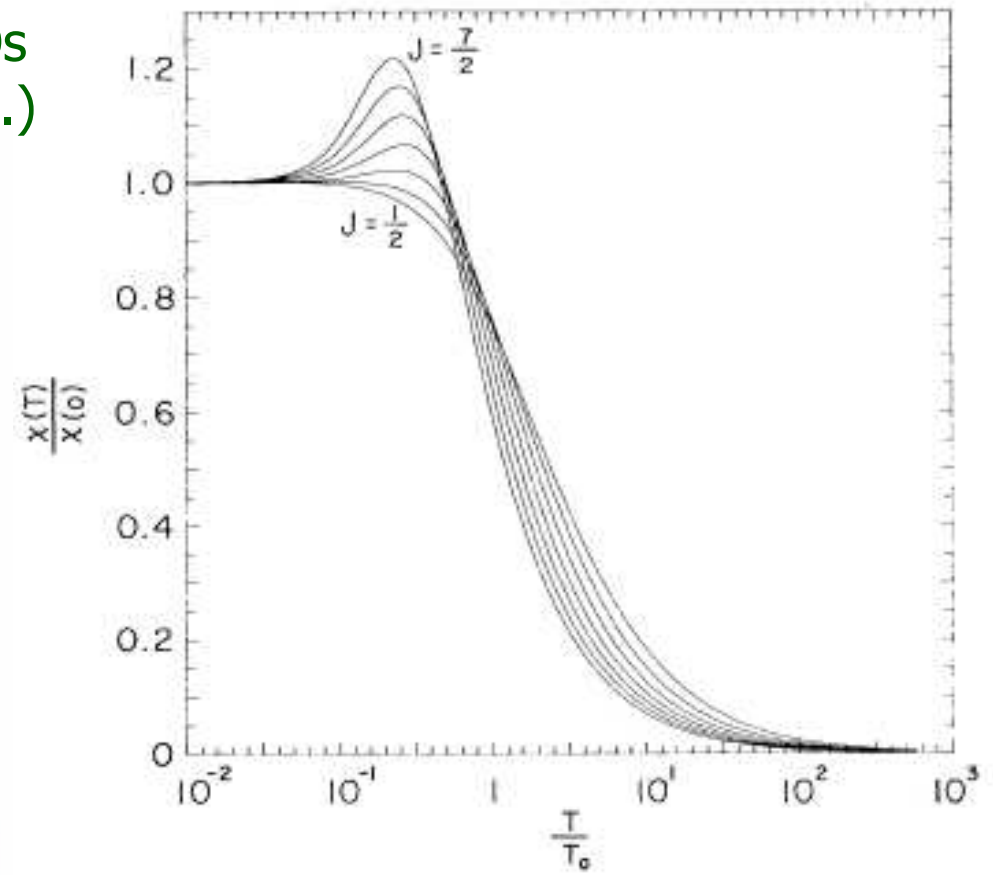
--If we assume that $T_{\Delta CEF}$ does not vary significantly (for the R site the nearest neighbors and next nearest neighbors are all Zn), then the T_K / $T_{\Delta CEF}$ ratio (and therefore the degeneracy) is higher for T = Fe and Ru then it is for T = Ir, Rh.

Torikachvili, et al. Proceedings of the National Academy of Sciences of the United States of America (2007), 104(24), 9960-9963.

Slightly more quantitatively, if we use Rajan's analysis of the Coqblin Schrieffer model, we can estimate the degeneracy by evaluating χ_{max} / χ(T~0 K).

From this analysis we find that T = Fe and Ru have J ~ 5/2 and T = Ir and Os have J ~ 3/2. (T = Rh is intermediate.)





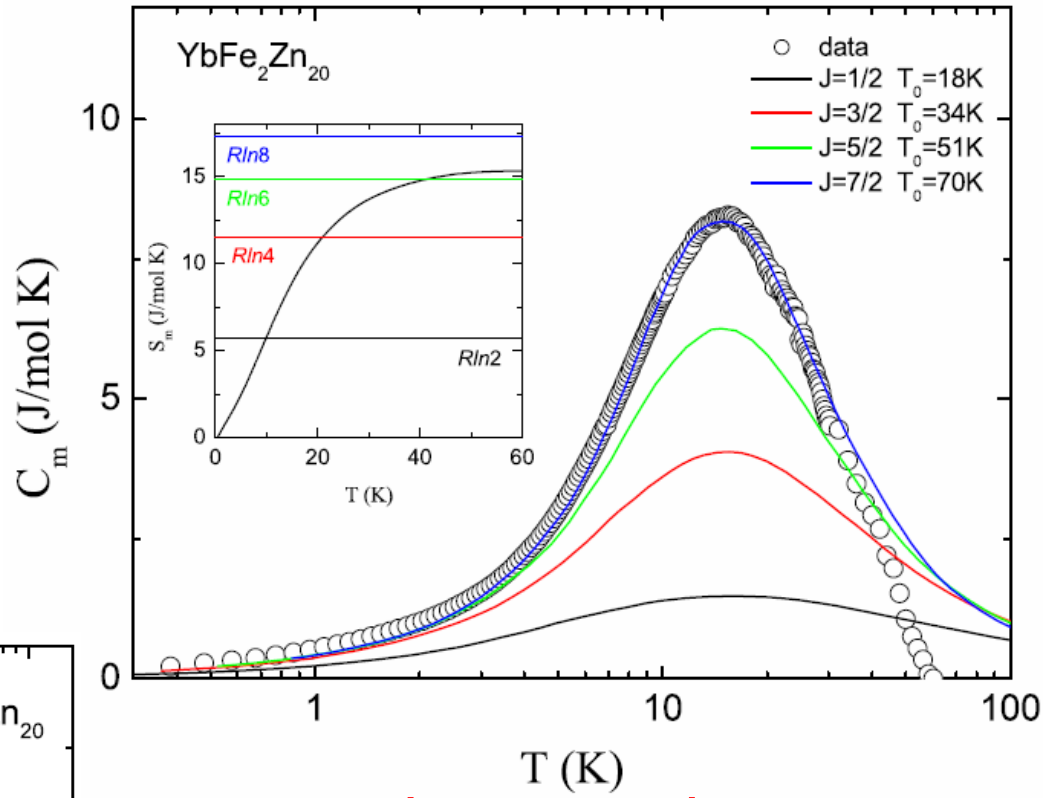
PHYSICAL REVIEW LETTERS

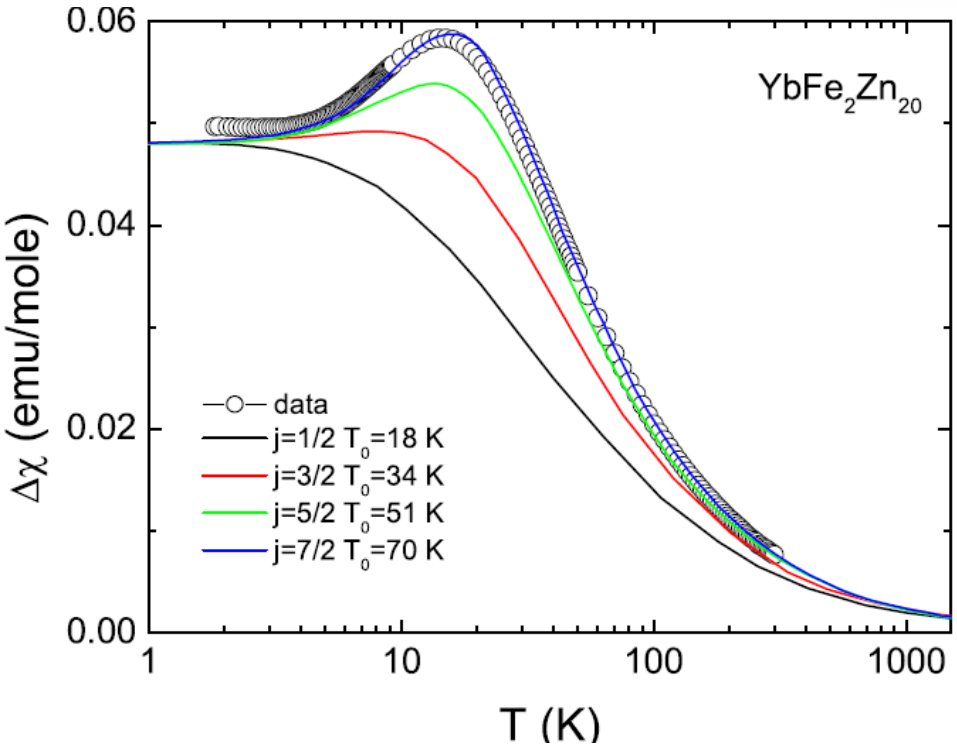
V. T. Rajan VOLUME 51, NUMBER 4 308 25 JULY 1983

Magnetic Susceptibility and Specific Heat of the Coqblin-Schrieffer Model

Torikachvili, et al. Proceedings of the National Academy of Sciences of the United States of America (2007), 104(24), 9960-9963.

We can pursue this even further (and much more formally) by fitting both the C_p and χ data to the Coqblin Schrieffer model.

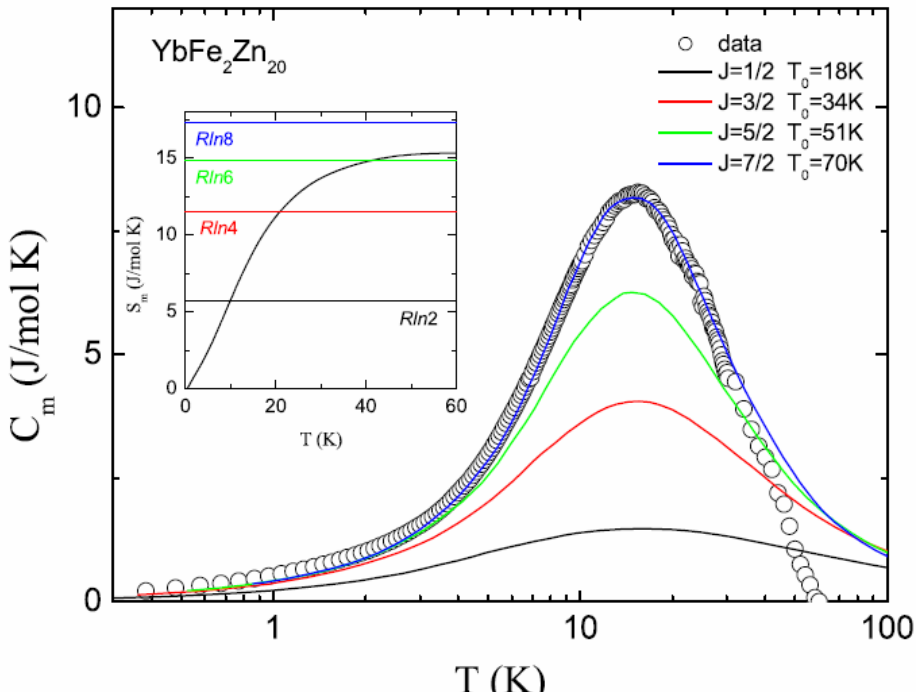


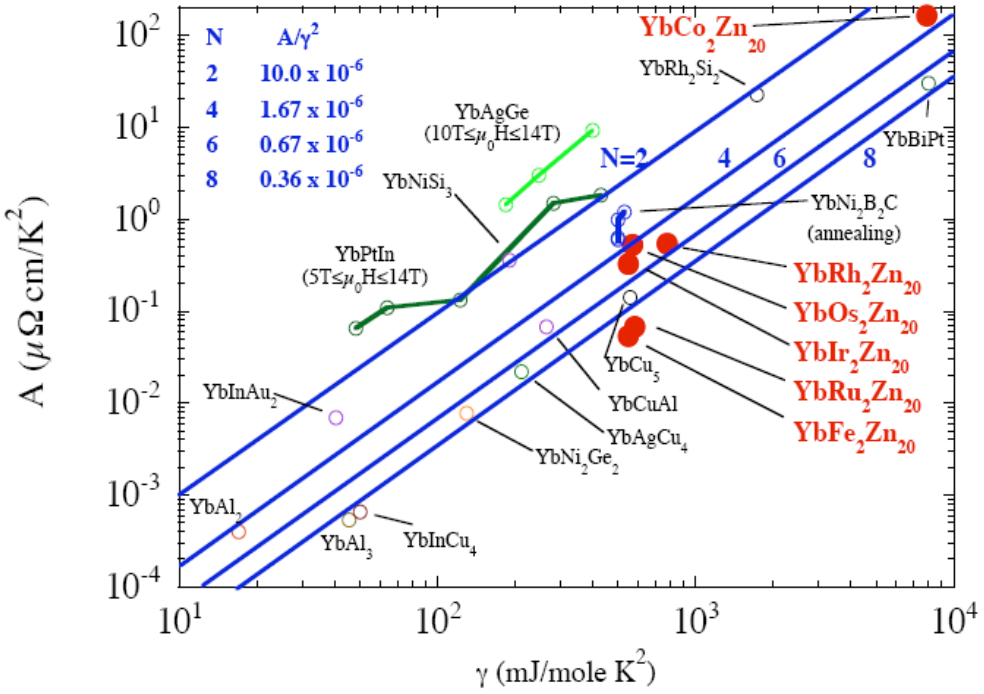


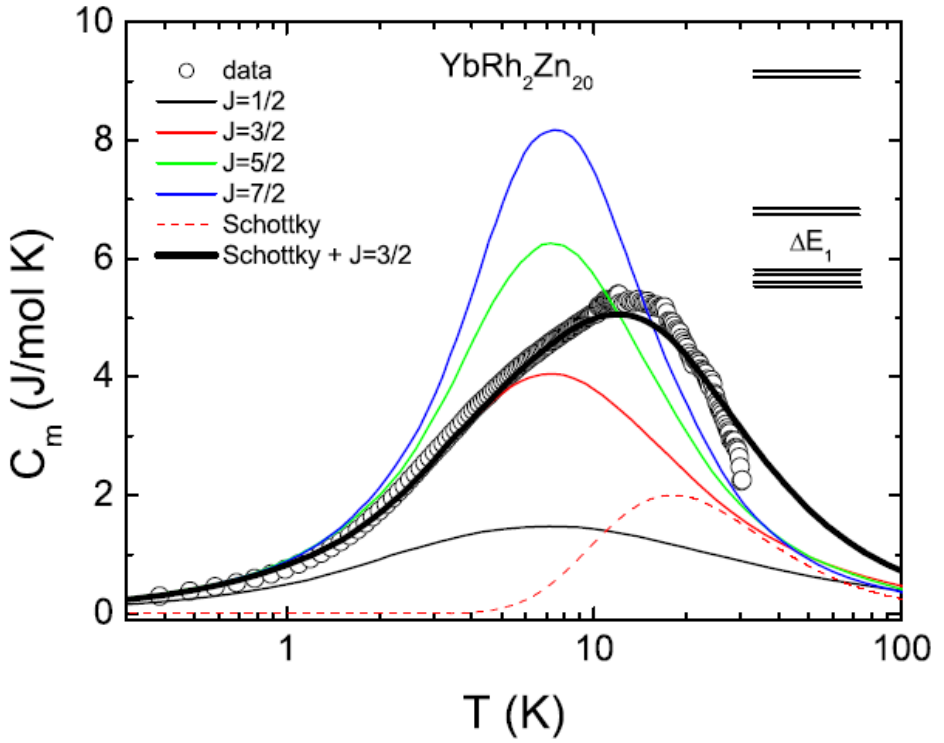
As can be seen, the degeneracy value of N = 8 (J = 7/2) from the K-W analysis (as well as the more informal analysis of χ) is clearly supported by both these data sets.

$YbFe_2Zn_{20}$ is a high degeneracy, N = 8, Kondo lattice.

On the other extreme $YbRh_2Zn_{20}$ $C_p(T)$ data has to be fit with N = 4 plus CEF Schottky anomaly.



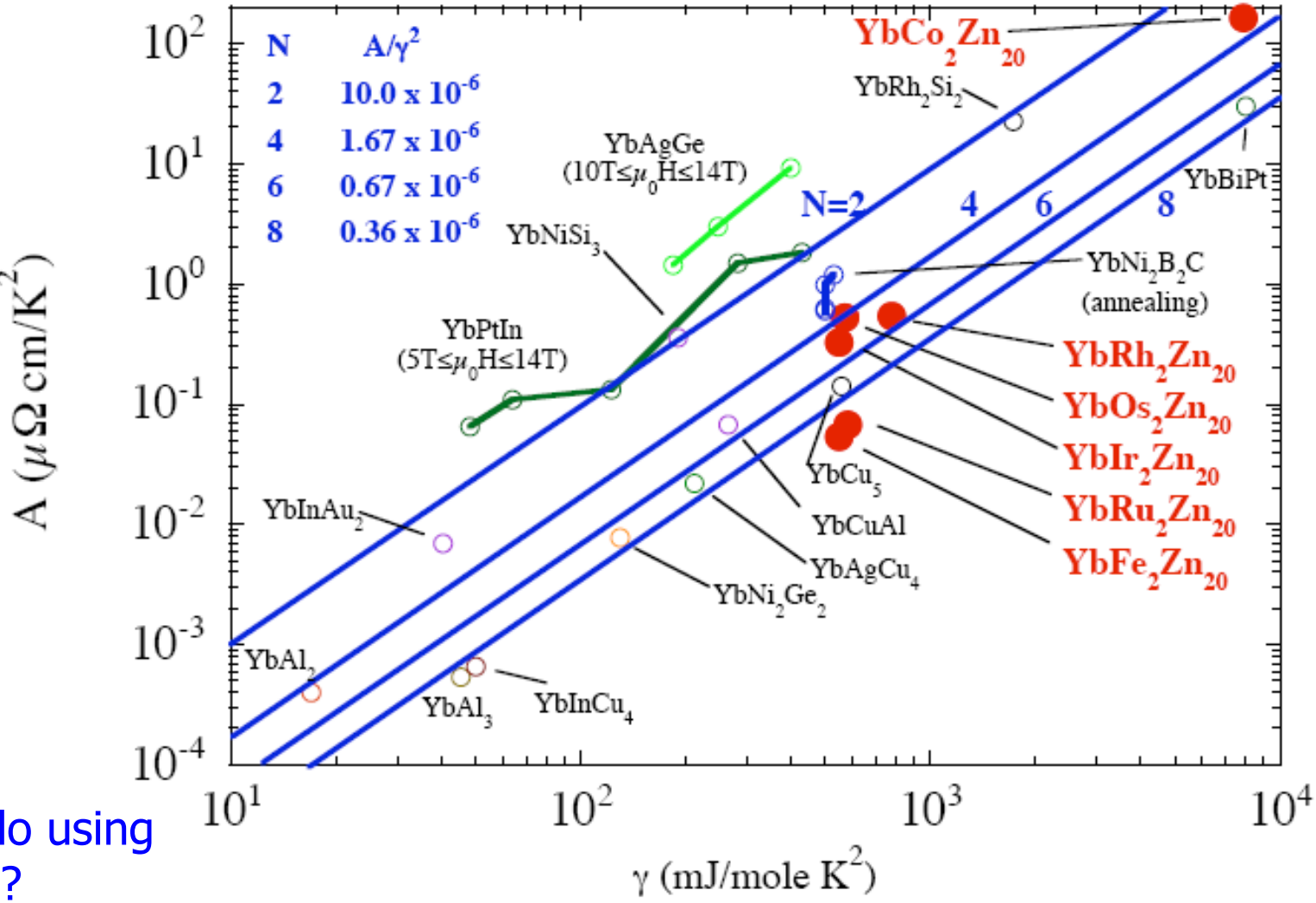




Torikachvili, et al. Proceedings of the National Academy of Sciences of the United States of America (2007), 104(24), 9960-9963.

Both qualitative and quantitative analysis support the conclusion we reach from the Kadawaki-Woods analysis: $YbFe_2Zn_{20}$ and $YbRu_2Zn_{20}$ both have higher Yb ion degeneracies at T_K.

The question of whether this is associated with the properties of $LuFe_2Zn_{20}$ and $LuRu_2Zn_{20}$ (Stoner-like) remains open.



What can we do using these N values?

Evaluation of T_K....This can be *easy* or **hard**.

From simple transfer of entropy arguments we get $\gamma T_K = R\ln(N)$

$$T_0 = \frac{\log(N)}{\gamma_{\rm imp}}.$$

More erudite and detailed analysis gives:

$$\gamma_{\rm imp} = \frac{\pi^2 w_N}{3T_K}\frac{N-1}{N}$$

$$w_N = \frac{e^{C+1-3/(2N)}}{2\pi\Gamma(1+1/N)}$$

J W Rasul and A C Hewson
J. Phys. C: Solid State Phys., **17** (1984) 2555–2573.

When I compared the easy with the profound, I was delighted to find that for physical values of N (8 or less), the easy, physically intuitive, approach is within 6% of the rather complex, formal one. !!!!

$$\kappa(N) \equiv \frac{T_K}{T_0} = \frac{\pi^2 w_N}{3}\frac{N-1}{N\log(N)}$$

N	$\kappa(N)$
2	0.97466
3	1.04484
4	1.03992
5	1.01667
6	0.98974
7	0.96344
8	0.93901
9	0.91670
10	0.89643

Thanks to J. Schmalian for checking my work on this.

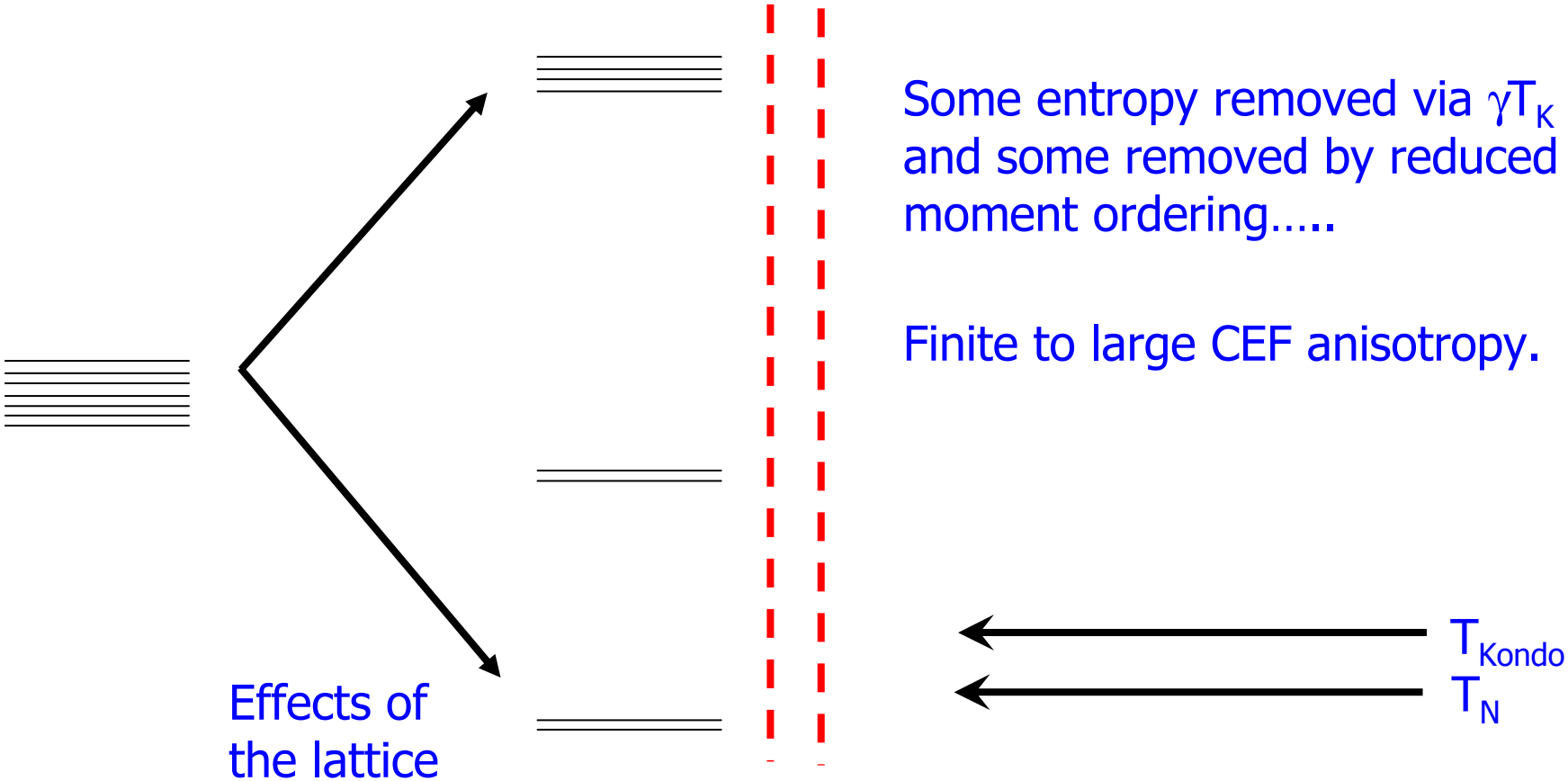
We can then use our γ and N values to extract T_K

TABLE I: Summary of structural, thermodynamic and transport data on YbT_2Zn_{20} compounds (T = Fe, Co, Ru, Rh, Os, Ir)

T	a Å	Θ K	μ_{eff} μ_B	χ_0 $\frac{10^{-3}cm^3}{mole}$	χ_{max} $\frac{10^{-3}cm^3}{mole}$	$T_{\chi_{max}}$ K	ρ_0 $\mu\Omega\ cm$	A $\frac{\mu\Omega\ cm}{K^2}$	RRR	γ $\frac{mJ}{mol\ K^2}$	WR	KWR $\frac{\mu\Omega\ cm\ mole^2\ K^2}{mJ^2}$	N	T_K K
Fe	14.062	-22.6	4.5	58.0	65.1	14.0	2.1	$5.4 \cdot 10^{-2}$ ($T \leq 11$ K)	31.2	520	1.2	$2.0 \cdot 10^{-7}$	8	33
Co	14.005	-4.3	4.3	415.1			21	165 ($T \leq 0.2$ K)	2.8	7900		$27 \cdot 10^{-7}$	4	1.5
Ru	14.193	-15.5	4.5	58.9	65.4	13.5	5.3	$6.8 \cdot 10^{-2}$ ($T \leq 11$ K)	10.9	580	1.1	$2.0 \cdot 10^{-7}$	8	30
Rh	14.150	-15.9	4.4	77.7	82.4	5.3	5.6	$54 \cdot 10^{-2}$ ($T \leq 6$ K)	11.8	740	1.3	$10.1 \cdot 10^{-7}$	4	16
Os	14.205	-19.18	4.5	60.0	60.7	11.5	17	$53 \cdot 10^{-2}$ ($T \leq 1$ K)	4.4	580	1.1	$15 \cdot 10^{-7}$	4	20
Ir	14.165	-23.8	4.4	55.9	56.3	6.5	8.8	$33 \cdot 10^{-2}$ ($T \leq 5$ K)	8.9	540	1.2	$11 \cdot 10^{-7}$	4	21

T_K is indeed higher for T = Fe and Ru compounds.
This confirms our qualitative analysis of χ(T) data.

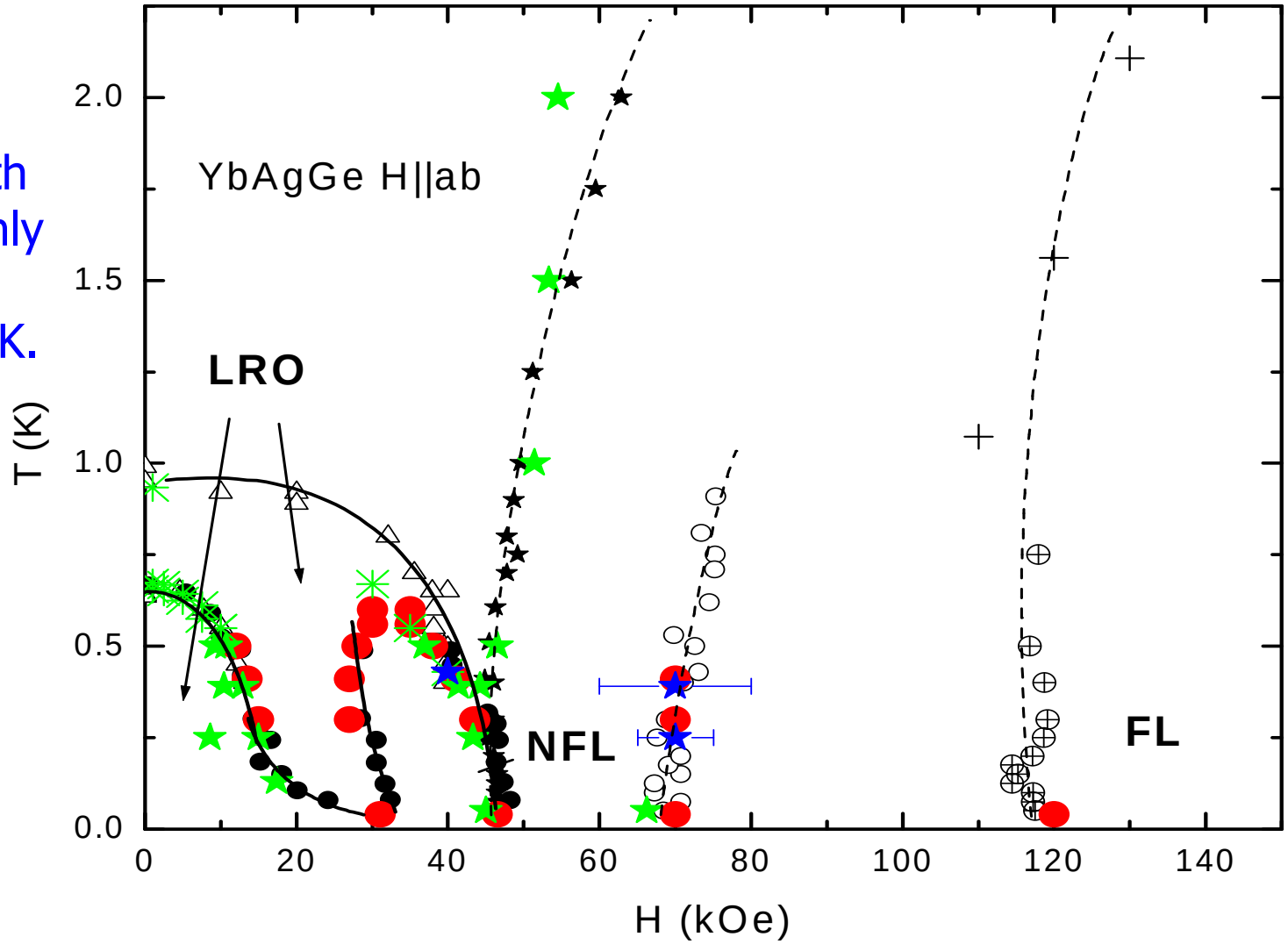
If the Kondo temperature and the magnetic ordering temperature can be brought a bit closer together (playing with the energy scales), then the system can be tuned from the local moment side to the correlated electron (heavy fermion) side.



For example, in YbAgGe the system can be tuned to a quantum critical point by application of modest magnetic fields….A physicists playground.

In zero field, the system orders with reduced, and highly anisotropic, moment below 1 K.

Application of H suppresses LRO and the evolution to a correlated Fermi liquid state can be studied.



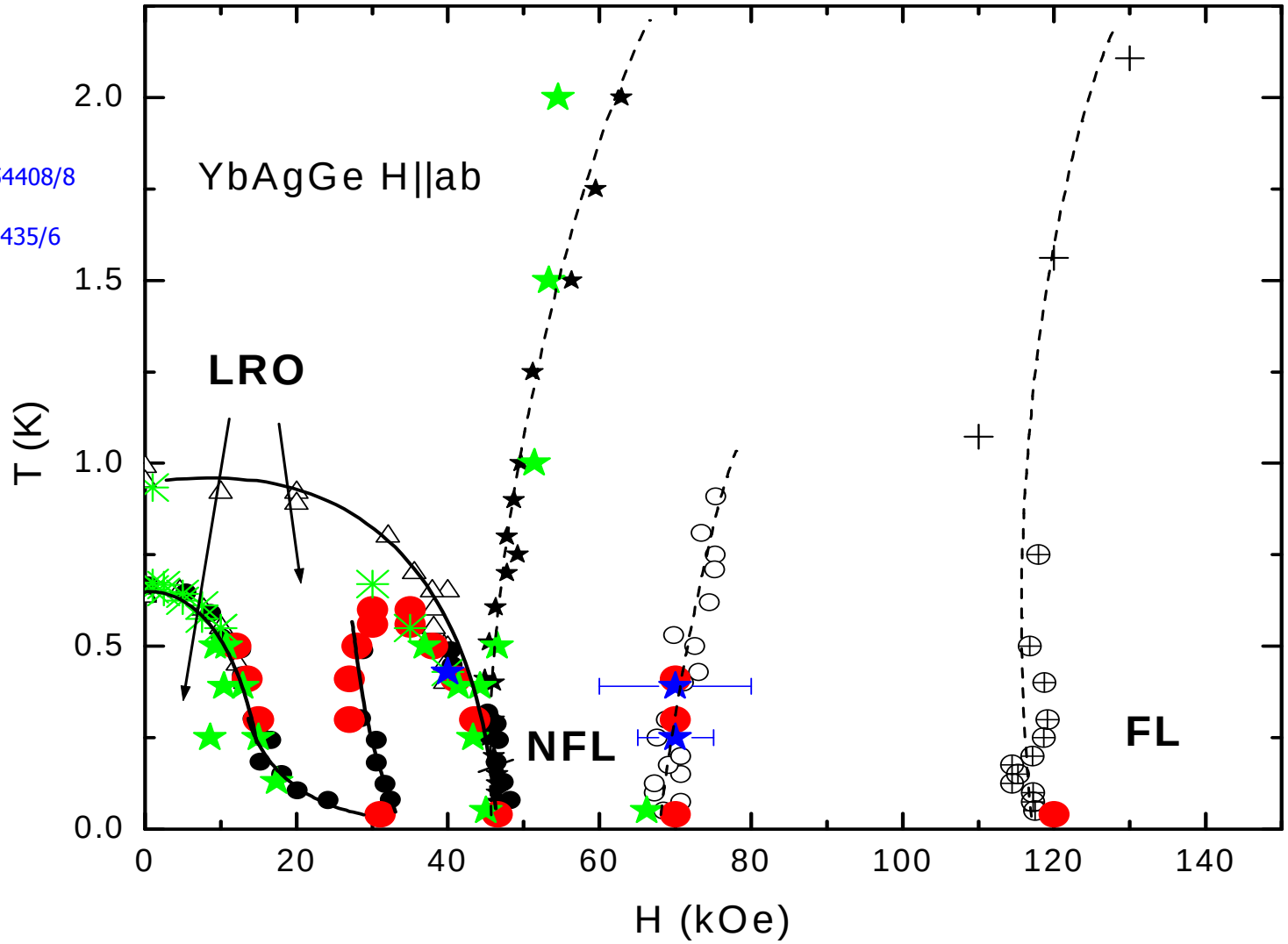
With quantum criticality we can fine tune rare earth systems from the local moment behavior we know and love into strongly, or moderately, correlated electron states that bear similarity of d-shell metals.

JMMM (2004), 277(3), 298-321

PRB (2004), 69(1), 014415/1-8

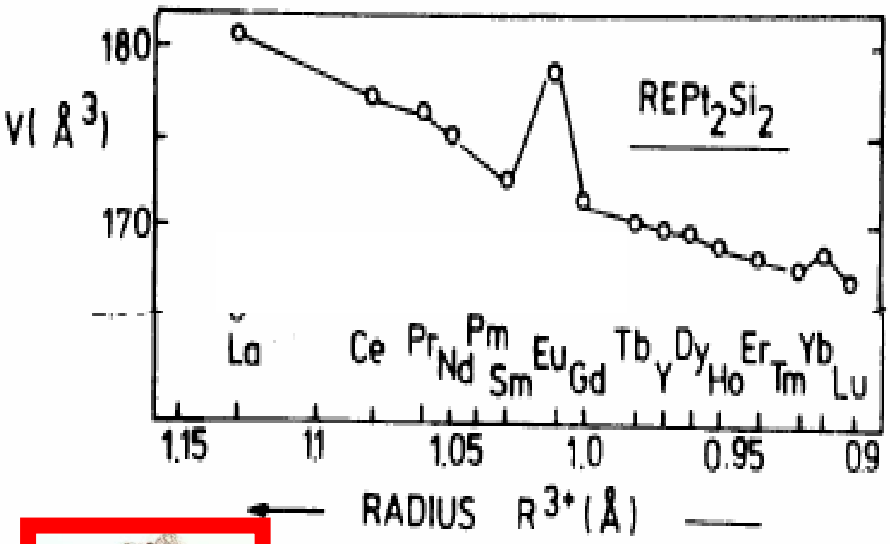
PRB (2005), 71(5), 054408/1-054408/8

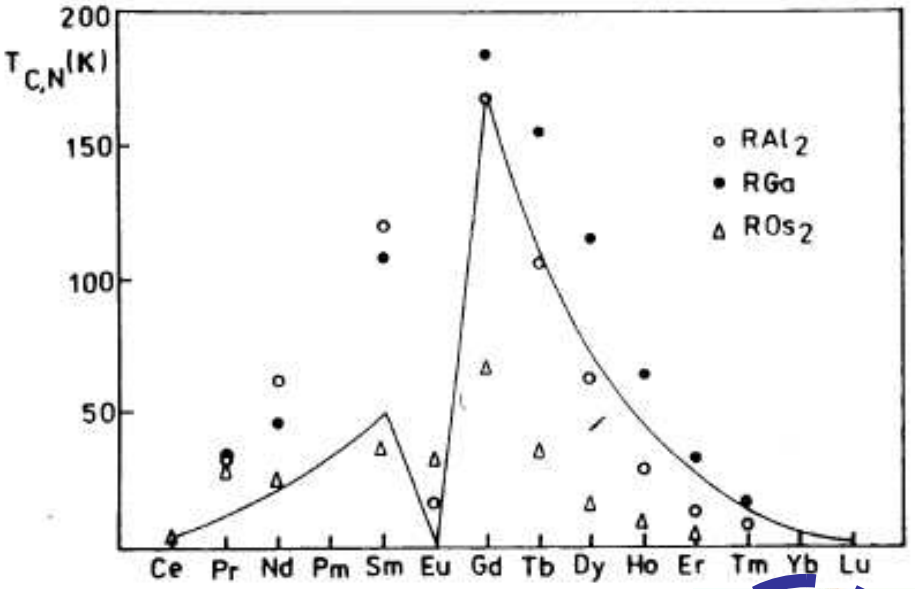
PRB (2006), 73(9), 094435/1-094435/6



If we think of decreasing field, we can study the birth of local moment behavior.

The purpose of this talk was to review how the rare earths can be viewed, and used by the physicist





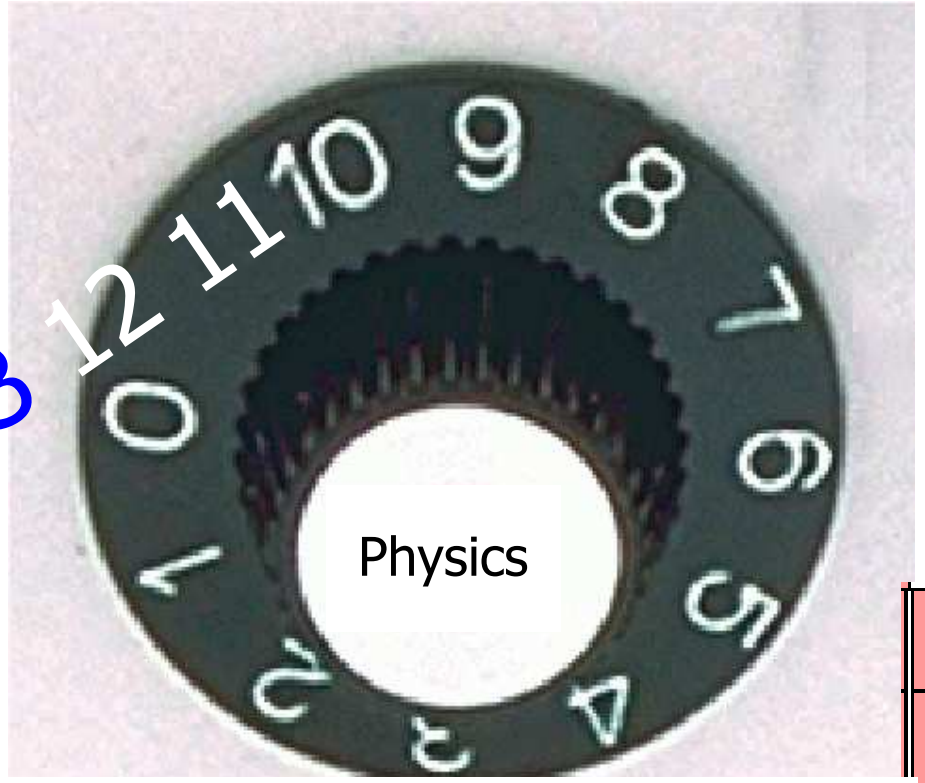
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb

57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.9	140.1	140.9	144.2	146.9	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0
	XXX hyb	XXX sng	3+ OK	XXX HOT	XXX Hund	XXX div	3+ OK	3+ OK	3+ OK	3+ OK	3+ OK	3+ OK	XXX hyb

The physicist sees a 17 position knob

That can be used to dial in magnetism
That can be used to control unit cell volume
That can be used to influence ansiotropy
That can be used to effect entropy
That can allow varying degrees of hybridization

It is this control and variety that draws the physicist to the rare earth series and compounds.



21 Sc 44.96														
39 Y 88.91														
57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0

Acknowledgements

Orson Welles once said that making films was like being a small child with a very expensive paint box. In a similar manner searching for new materials and growing single crystals of a wide variety of compounds requires a adequate and flexible materials budget. We gratefully acknowledge the US Department of Energy, Office of Basic Energy Sciences. Their unflagging support has made all of this research possible.

Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. The work at Ames was supported by the Director of Energy Research, Office of Basic Energy Sciences.


That's All Folks