



The Design, Discovery, Growth and Physical Properties of Novel Intermetallic Compounds

CHARACTERIZATION

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In this lecture we will review basic types measurements:

Resistivity, ρ

Specific heat, C_p

Magnetization, M , and magnetic susceptibility, χ .

and how to use them for the identification of basic phase transitions and ground states such as:

Antiferromagnetic

Ferromagnetic

Superconductor

Metal-to-Insulator

Charge Density Wave

Meta-magnetic

We will use contemporary compounds and review published data.



Resistivity / Resistance

We can look at this in two simple ways:

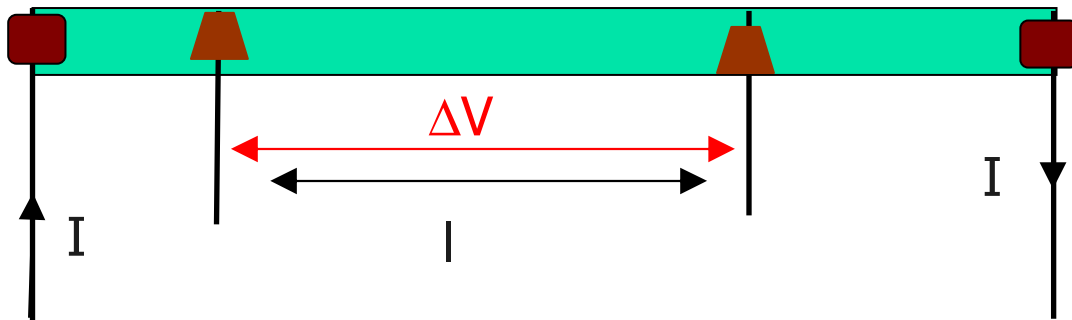
$$\sigma = ne^2\tau/m \quad \rho = 1/\sigma$$

In this case we can make inferences about n and / or τ

Another, slightly more sophisticated formula is the Kubo formula:

$$\sigma = (1/4\pi^3)(e^2/3\hbar) \int \Lambda dS_F \quad (\text{which is basically an integral of the electronic mean free path, } \Lambda, \text{ over the Fermi surface})$$

NOTE: the measured electrical resistivity will contain an impurity scattering term, ρ_0 which appears additively. This is often associated with chemical impurities as well as a variety of structural defects.



$$R = \Delta V/I$$

$$R = \rho l/A$$

Care in measuring ΔV , I , l and A is, of course, needed



Resistivity / Resistance

For a simple metal the resistivity can often be modeled by:

$$\rho = f(T) + \rho_0 \text{ and}$$

Where $f(T) \sim AT^2$ at lowest T

and $f(T) \sim BT$ at intermediate T

ρ_0 is the manifestation of the finite nature of Λ .

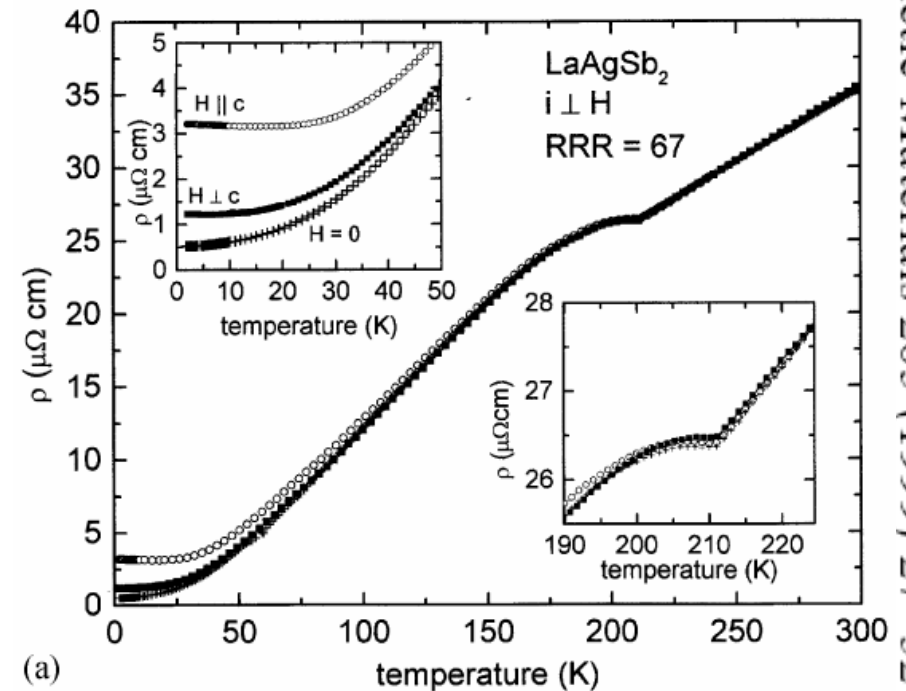
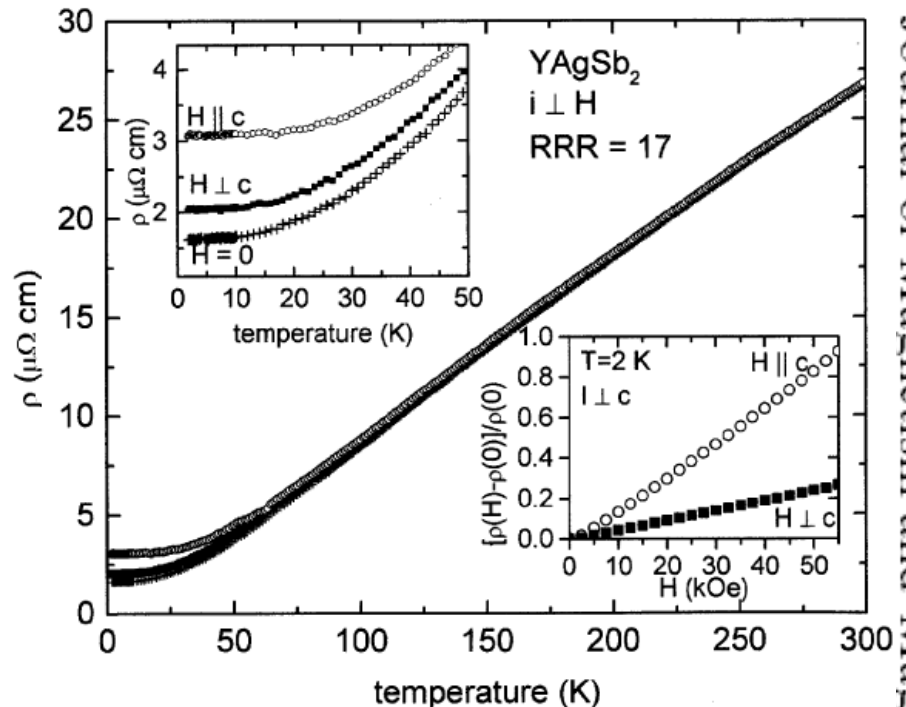
The residual resistivity ratio: RRR, is a measure of how defect free (or defected) a metallic sample is.

$$\text{RRR} = \rho(\text{high } T) / \rho(\text{low } T)$$

$$\text{Often } \text{RRR} = \rho(300 \text{ K}) / \rho(2 \text{ K})$$

NOTE: RRR is also $R(\text{HT})/R(\text{LT})$ since factors of l/A cancel out.

High RRR means low ρ_0 .



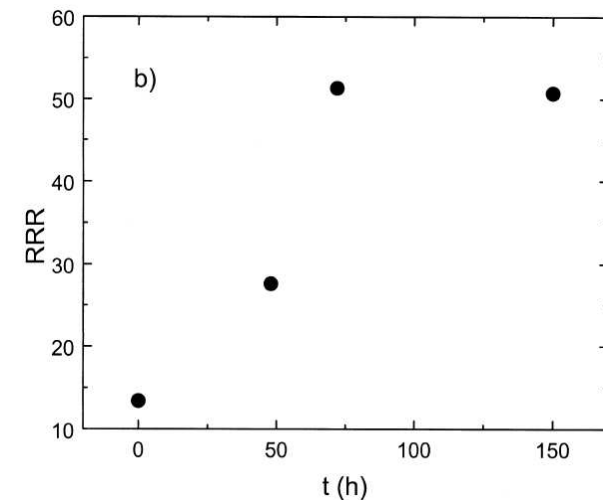
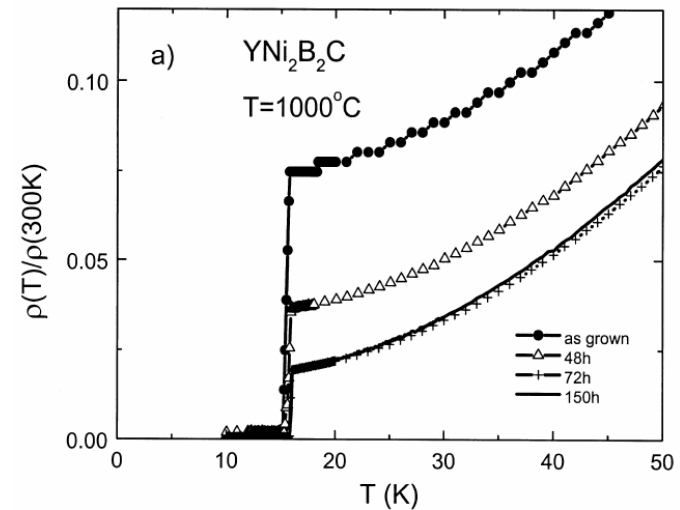
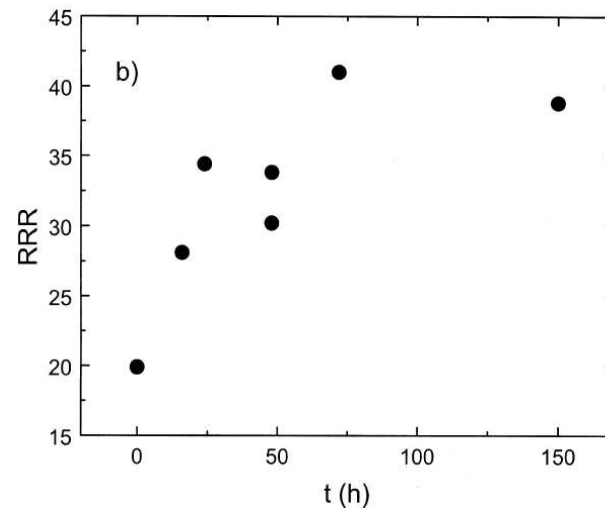
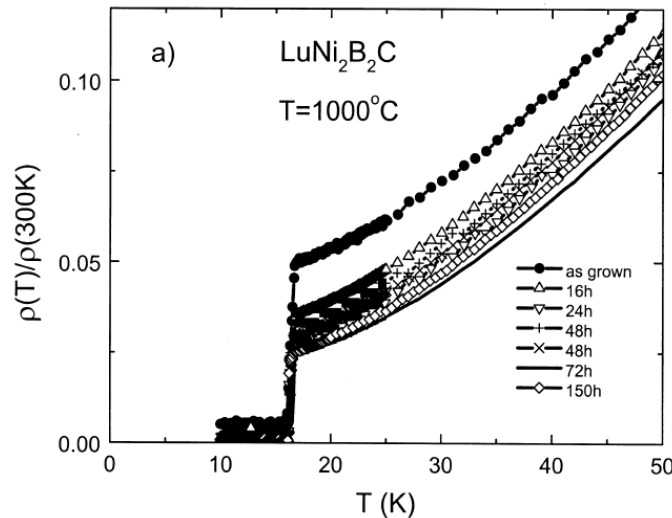
(a)



Resistivity / Resistance

If the defect density of a compound can be controlled then ρ_0 (and therefore Δ) can be systematically changed, leading to a constant off-set in resistivity curves. This can be done by judicious annealing of the sample (in some cases).

Superconductivity is easy to spot in $\rho(T)$ data since it manifests as a sudden drop in ρ to zero.



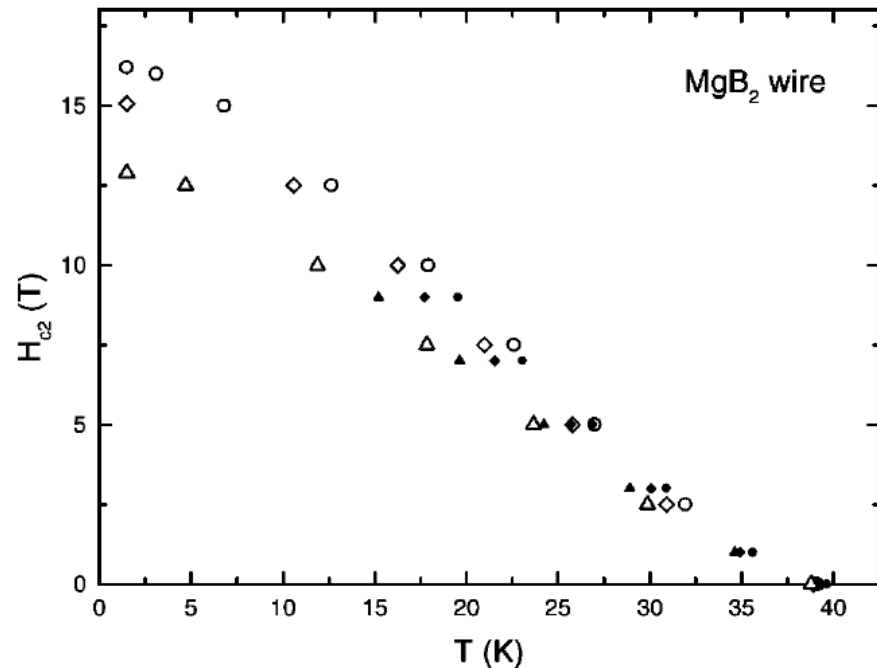
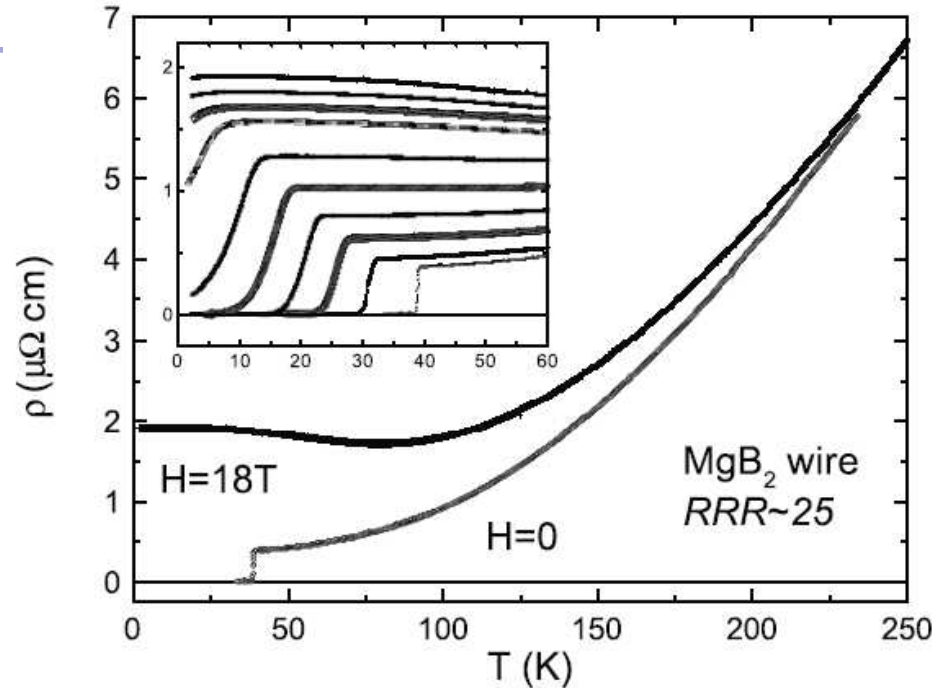


Resistivity / Resistance

Resistivity measurements can be used to learn about the superconducting state, for example in MgB_2 .

$\rho(T, H)$ data can be used to delineate the superconducting / normal phase boundary: $H_{c2}(T)$.

It is important to clearly state the criterion or criteria used to determine a transition point. In this case we illustrated the effect of using an onset, mid-point, and off-set criterion.



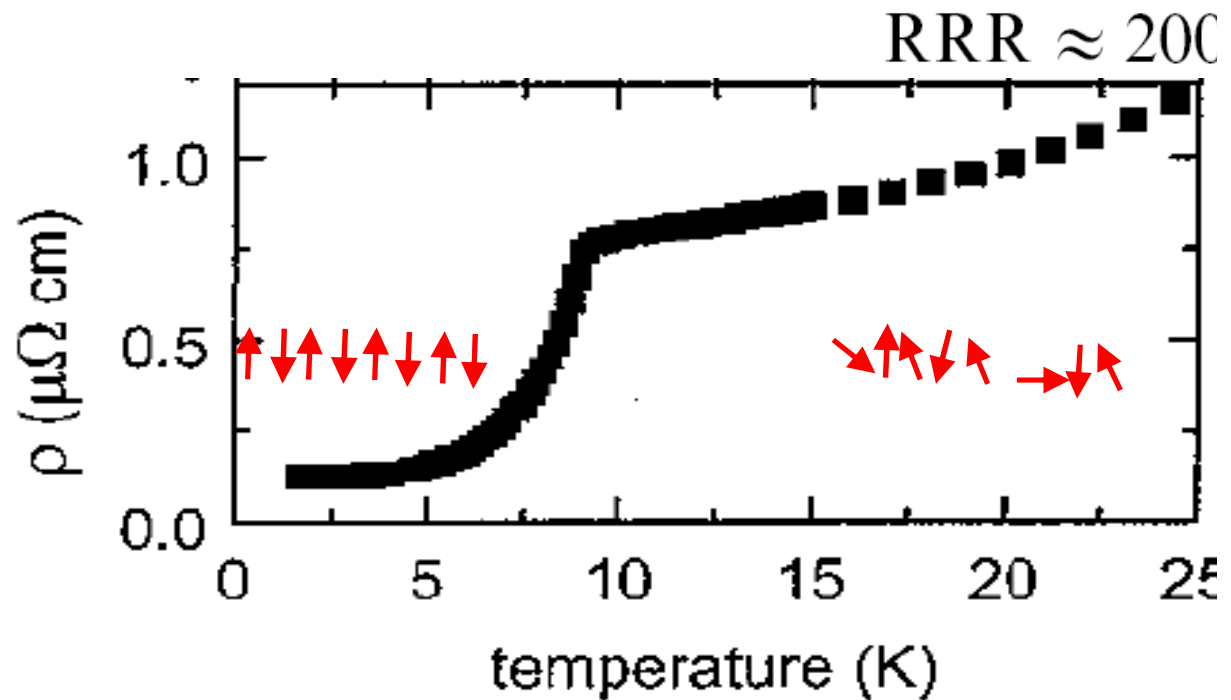
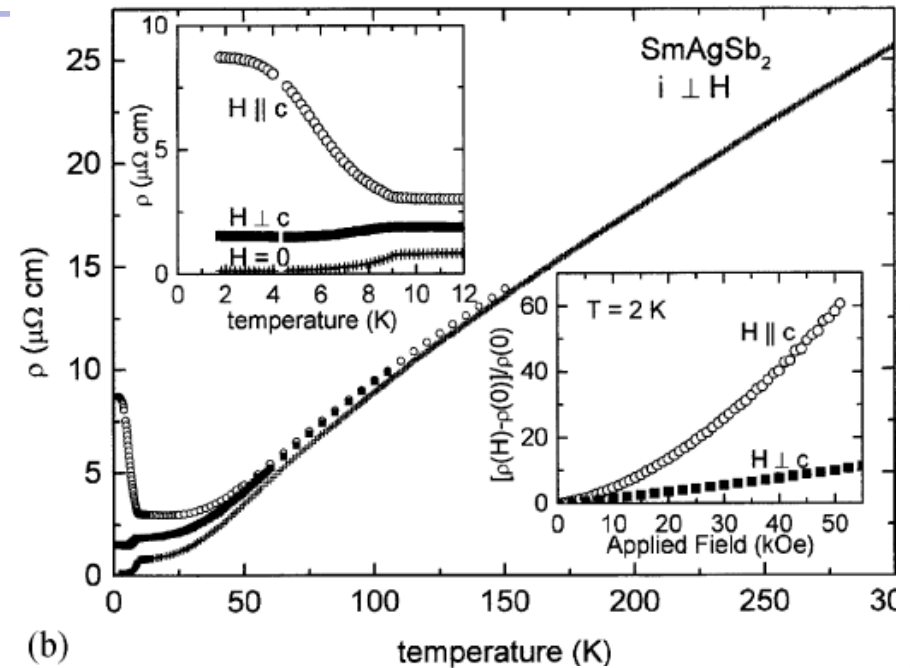


Resistivity / Resistance

Effects of local moments,
ordered as well as disordered.

ρ_0 decreases with increased order.
Structurally this means less defects.
The conduction electrons can also
couple to localized magnetic
moments, such as on rare earths.

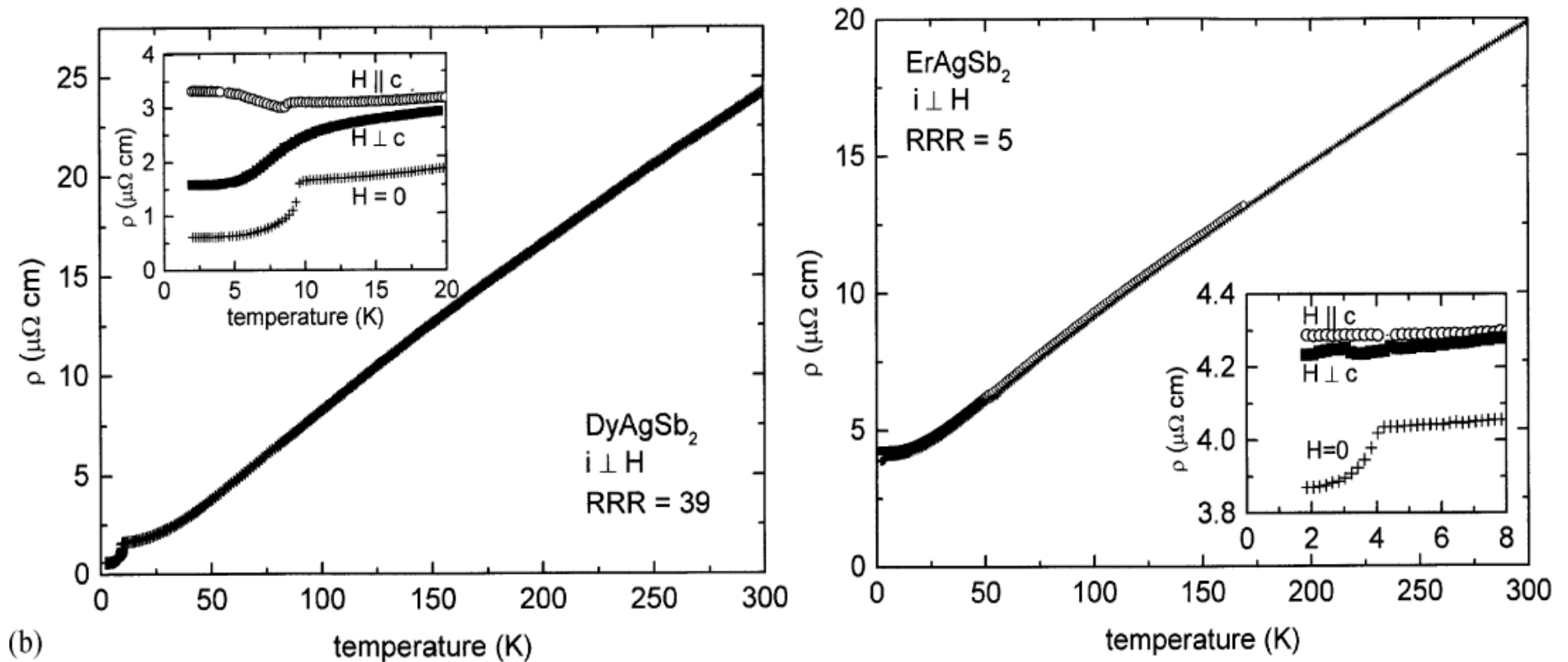
When the moments
change from disordered
(paramagnetic) to
ordered (ferromagnetic,
antiferromagnetic, or
more complex order)
there is a decrease in
scattering. This is called
a loss of spin-disorder
scattering.





Resistivity / Resistance

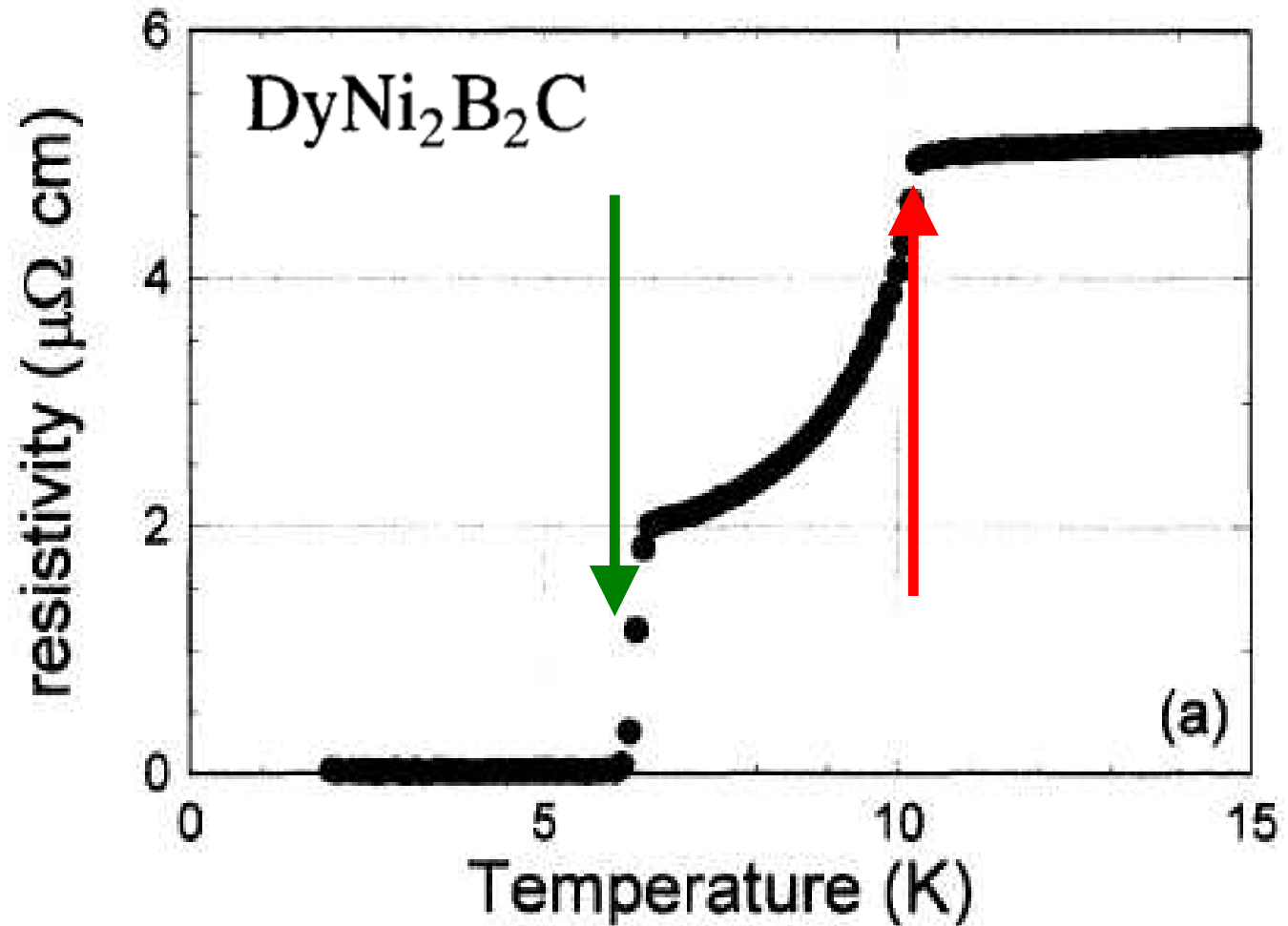
Loss of spin disorder scattering can be seen in high RRR samples as well as in low RRR samples, but it does get harder and harder to see as ρ_0 increases (RRR approaches unity).





Resistivity / Resistance

Multiple transitions can be easily detected and identified: In this case we have a rare example of $T_N \sim 10$ K with the loss of spin disorder scattering, followed at lower temperatures by $T_c \sim 6$ K and a total loss of resistivity.



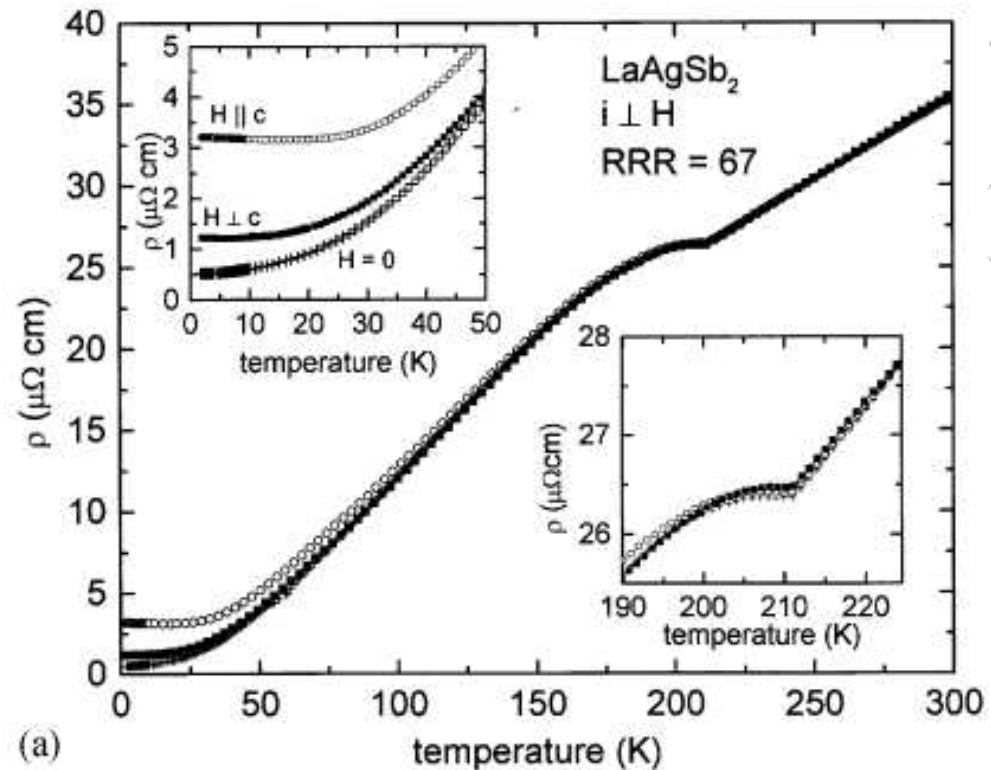
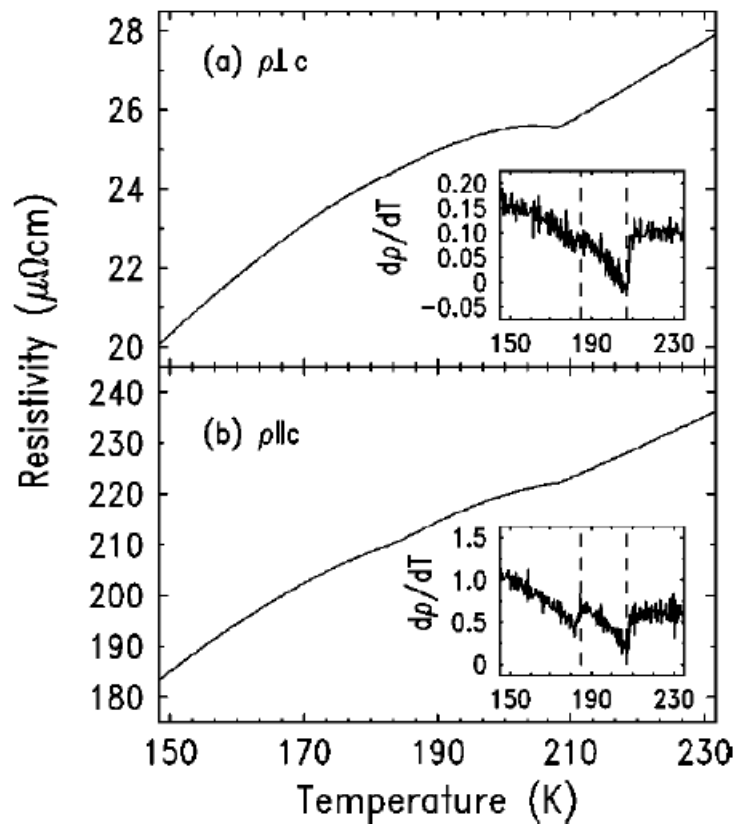


Resistivity / Resistance

Resistivity is also very sensitive to changes in the Fermi Surface:

$$\text{Kubo formula: } \sigma = (1/4\pi^3)(e^2/3\hbar)\int \Lambda dS_F$$

This can be seen in CDW (and SDW) transitions, where nested parts of the Fermi surface become gapped below T_{CDW} . This leads to an decrease in σ due to a decrease S_F . For a partial gapping of the F.S. the sample remains metallic and ultimately returns to $\rho(T)$ with positive slope.



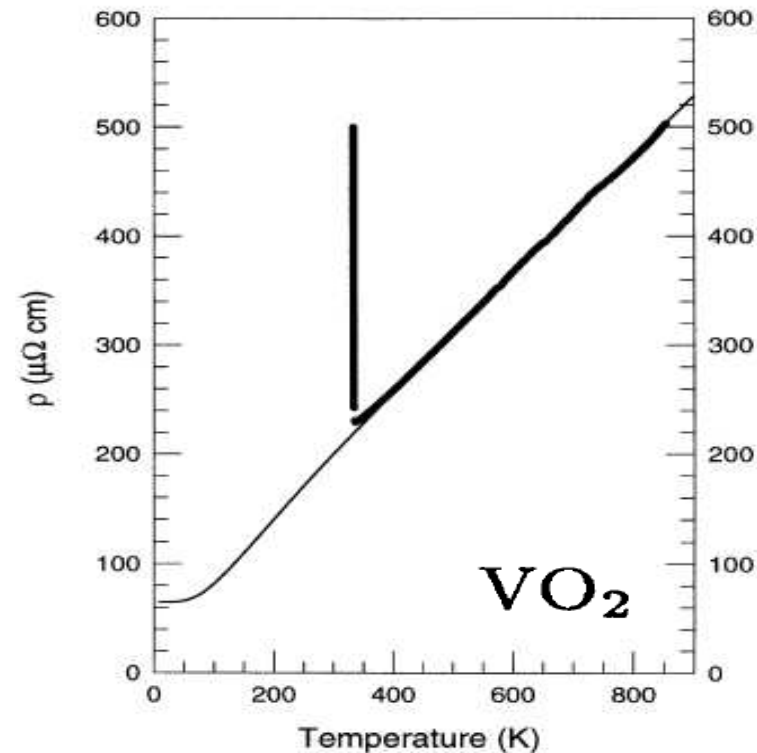
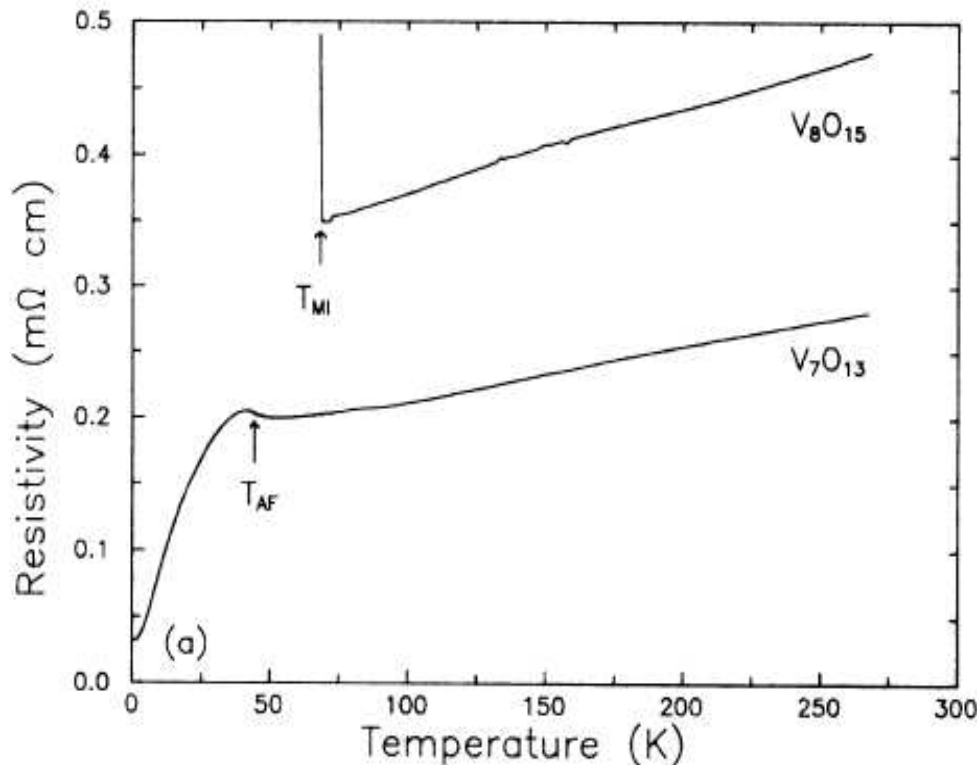


Resistivity / Resistance

If the Fermi surface is fully gapped, S_F goes to zero, then the resistivity becomes infinite. Kubo formula: $\sigma = (1/4\pi^3)(e^2/3\hbar)\int \Delta dS_F$

Another way of thinking of this is that the number of carriers, n , goes to zero:
$$\sigma = ne^2\tau/m \quad \rho = 1/\sigma$$

This is a metal-to-insulator transition and is seen in some CDW / SDW systems as well as several 3-d transition metal oxide systems.





Specific heat

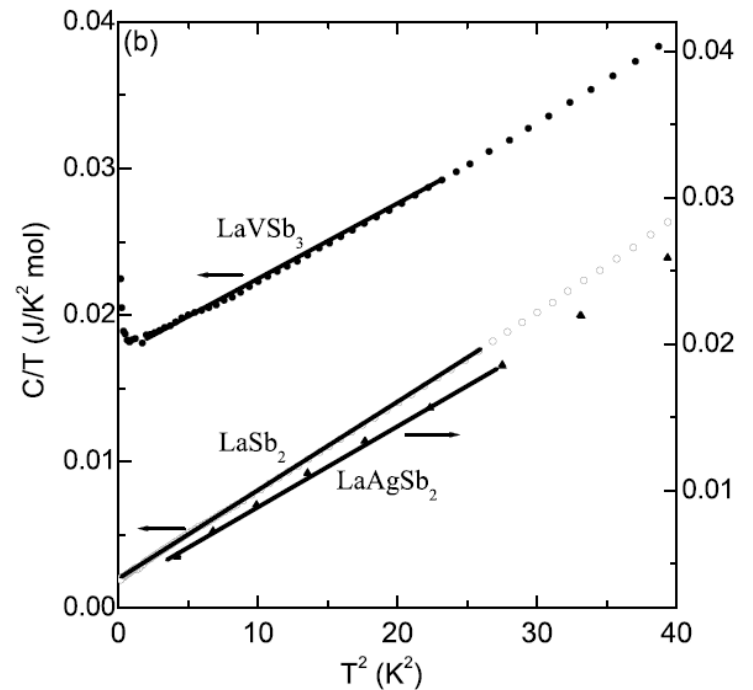
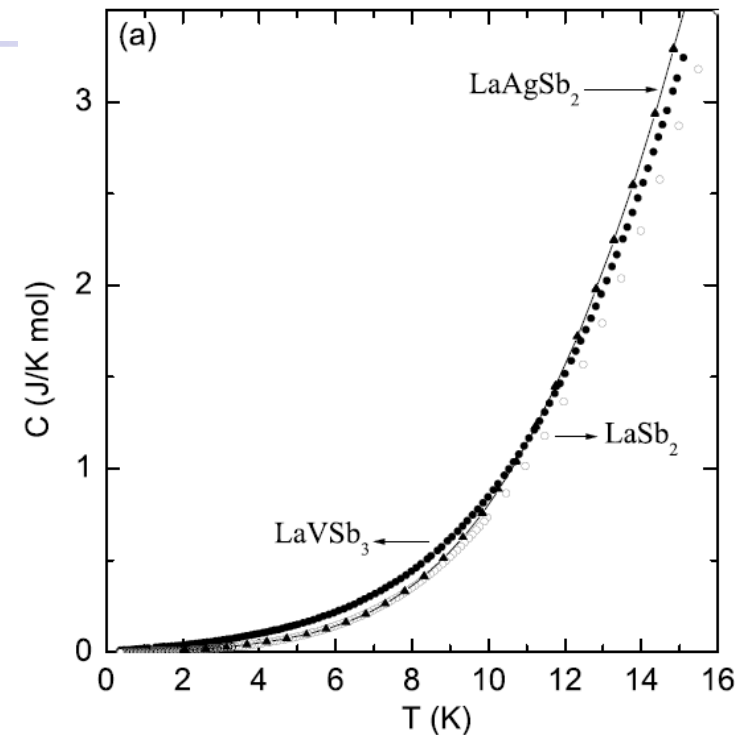
In a non-magnetic sample, specific heat can provide information about the electronic and vibrational excitations modulo $k_B T$.

At low temperatures the specific heat of a metal can be modeled as

$$C_p = \gamma T + \beta T^3$$

A plot of C/T versus T^2 allows for the clean separation of γ and β .

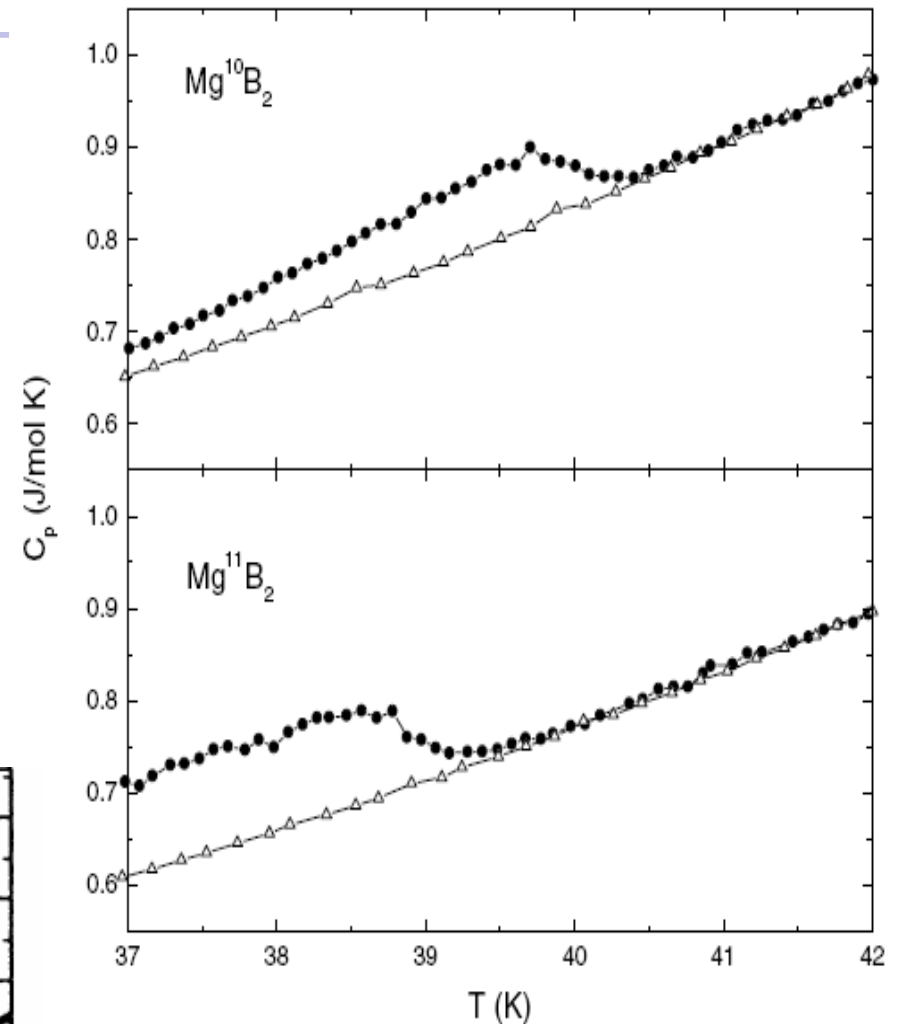
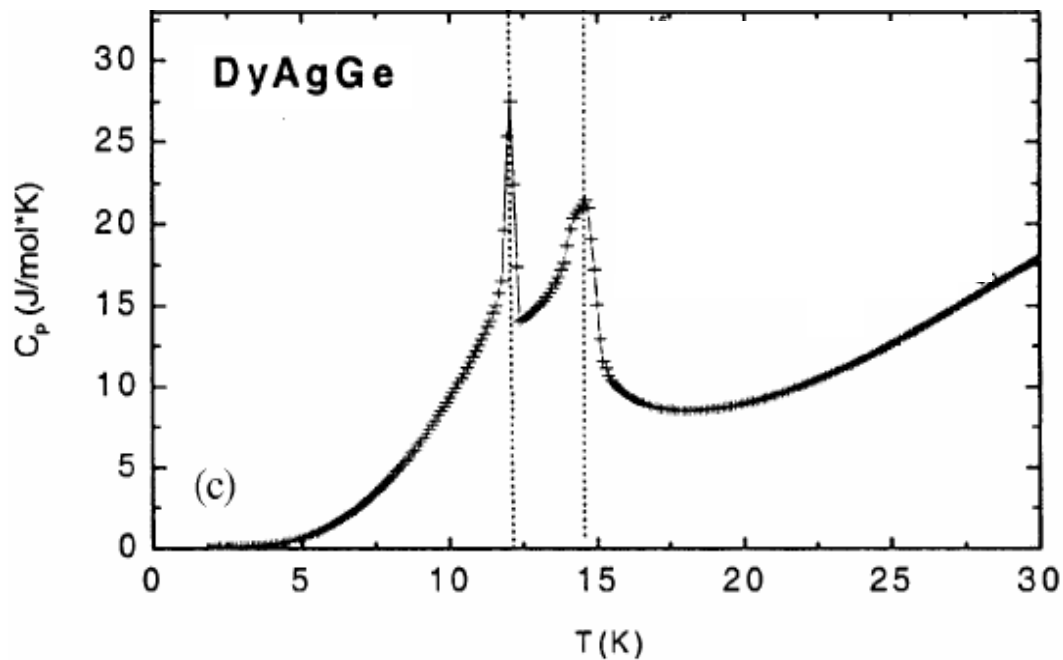
In simple models γ is proportional to $N(E_F)$ or, alternately, the electron mass, and β is proportional to the Debye temperature and the characteristic frequency of lattice vibrations.





Specific heat

Specific heat can also be used to locate and characterize phase transitions. As seen earlier, we can suppress T_c with an applied field, so the C_p feature can be more clearly seen via comparison to the non-superconducting (in high applied magnetic field) compound.



Local moment ordering can be seen even more clearly (larger entropy). Shown here are a series of transitions in antiferromagnetic DyAgGe.

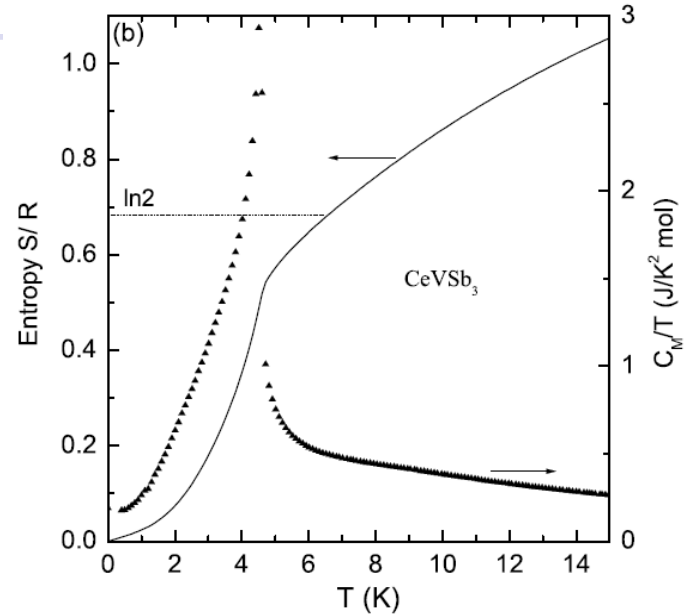
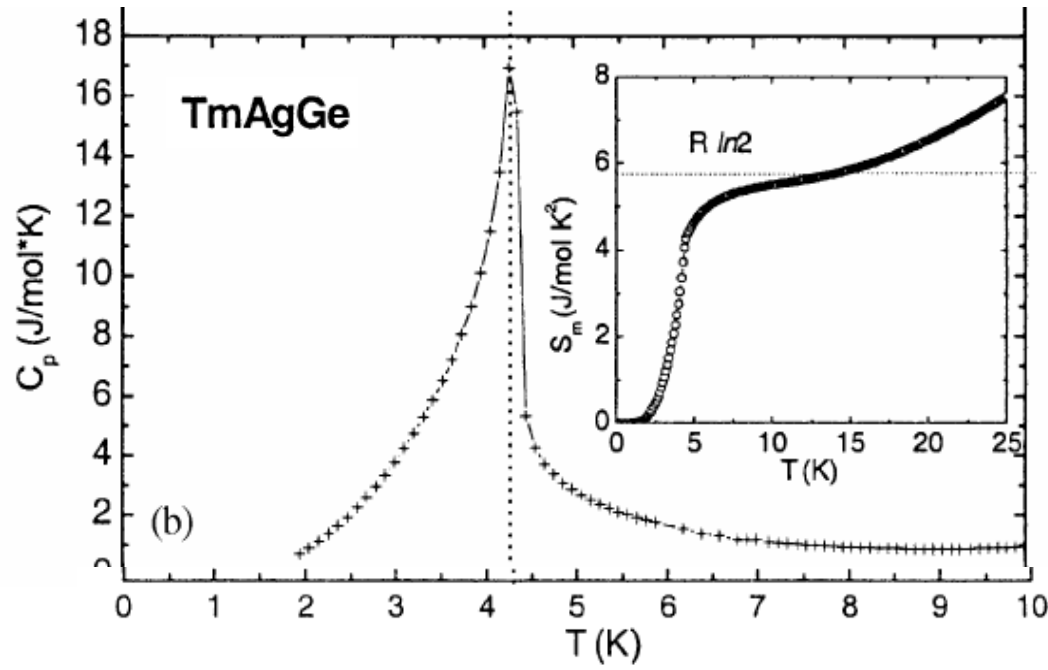


Specific heat

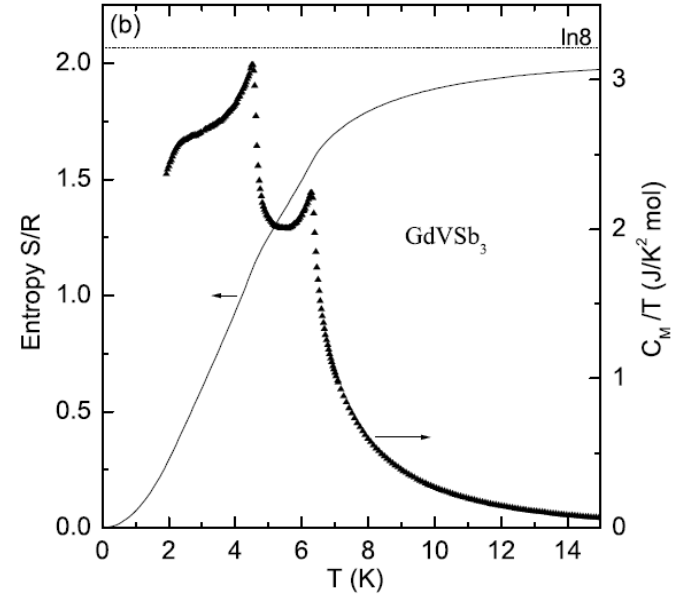
Specific heat is intimately related to entropy

$$\int (C_p/T) dT = S$$

This means that we can determine how much entropy is associated with a given state. For magnetic systems we need to use the magnetic C_p . We often do this by subtracting off the $C_p(T)$ data from a non-magnetic analogue (e.g. LuAgGe from TmAgGe).



For these local moment systems $S \sim R \ln D$

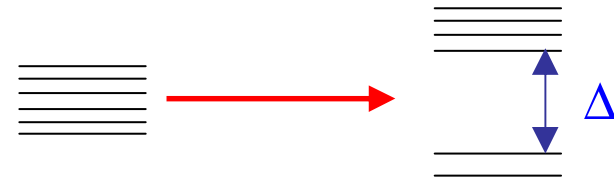




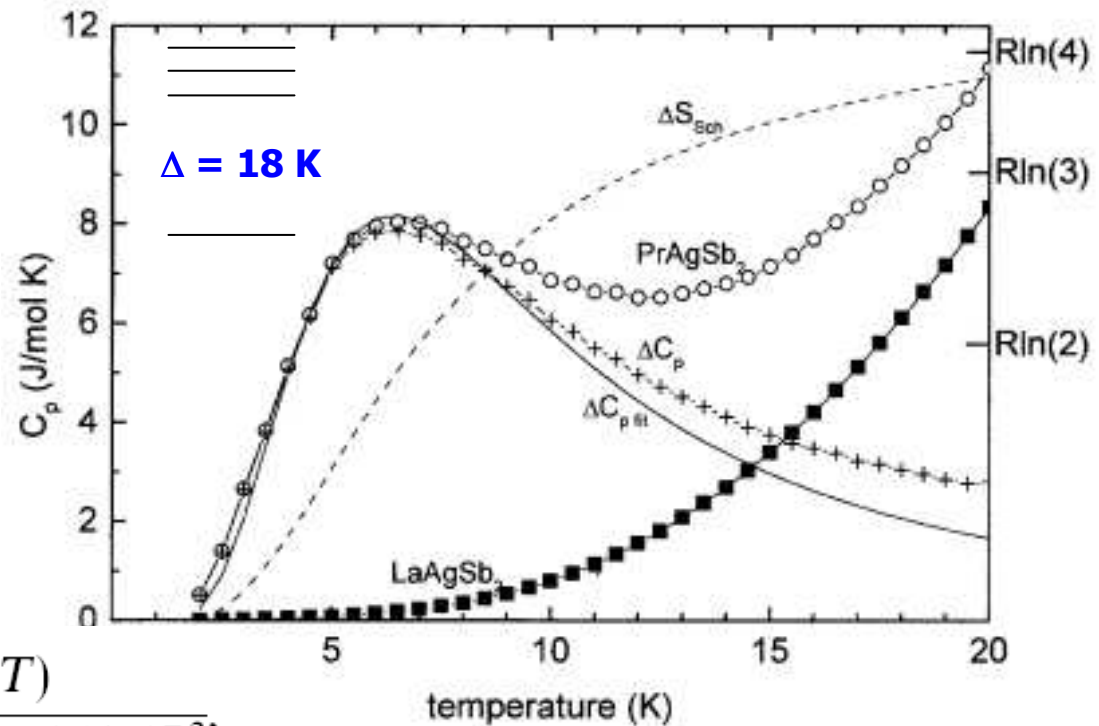
Specific heat

Given the Hund's rule, groundstate multiplet J we would expect $R \ln(2J + 1)$ entropy associated with the magnetic state. This is what we find for Gd: ($S = 7/2$, $L = 0$ and $J = 7/2$) $\Delta S \sim R \ln(8)$. For other rare earths the spin-orbit coupling give rise to crystalline electric field (CEF) splitting.

e.g.: Ce ($J = 5/2$) in cubic point symmetry



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.



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



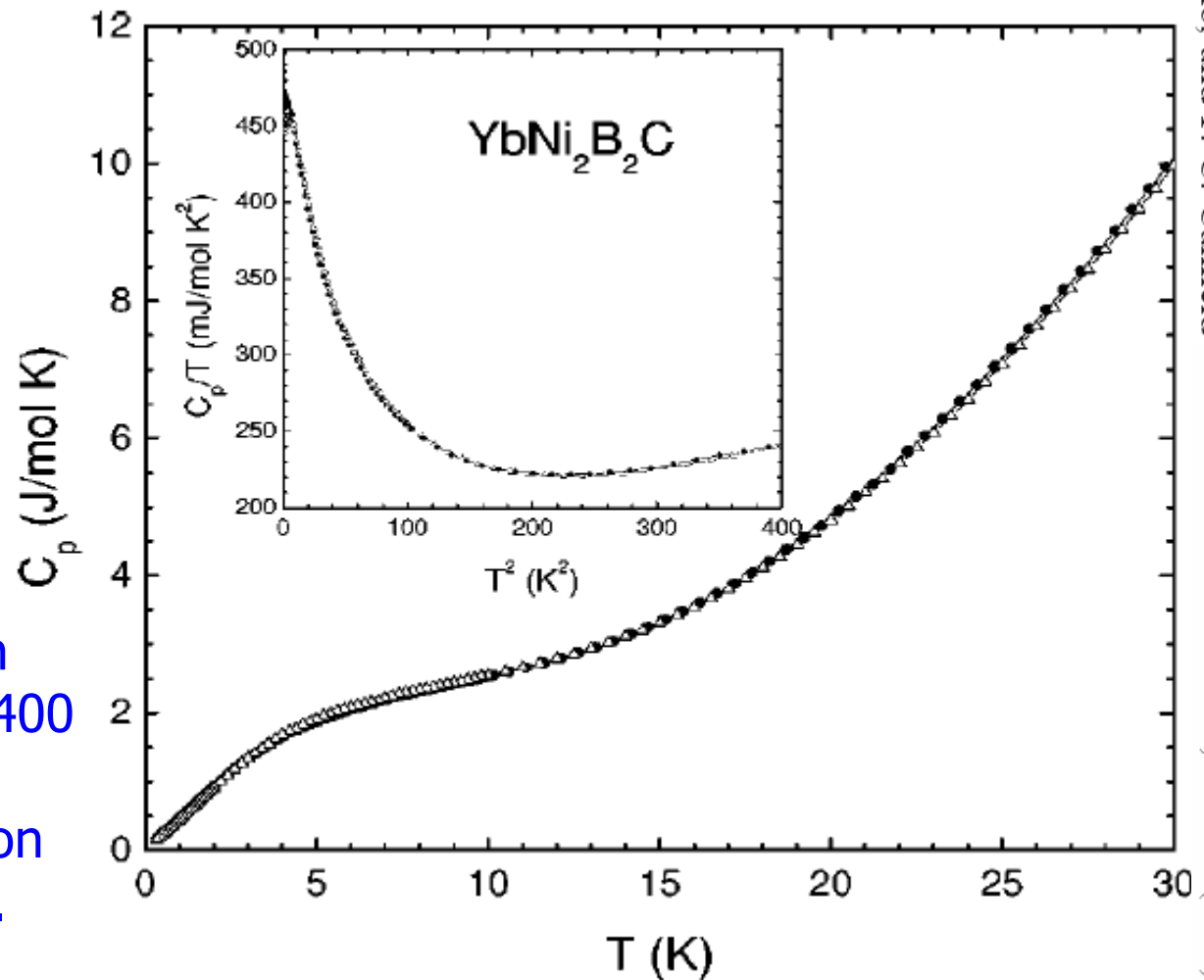
Specific heat

The electronic specific heat can be used as a measure of the electron effective mass, based on the free electron result of

$$\gamma = (\pi^2/3) * k_B^2 T * N(E_F) = k_B^2 T * (mk_F/3\hbar^2)$$

Heavy Fermions are compounds with exceptionally high values of γ for $T < T_K$, the Kondo temperature.

Strictly speaking, they are defined as compounds with $\gamma > 400$ mJ/mol-K², about 400 times the value of γ for Cu. Large γ means large electron mass, ergo, heavy fermion.



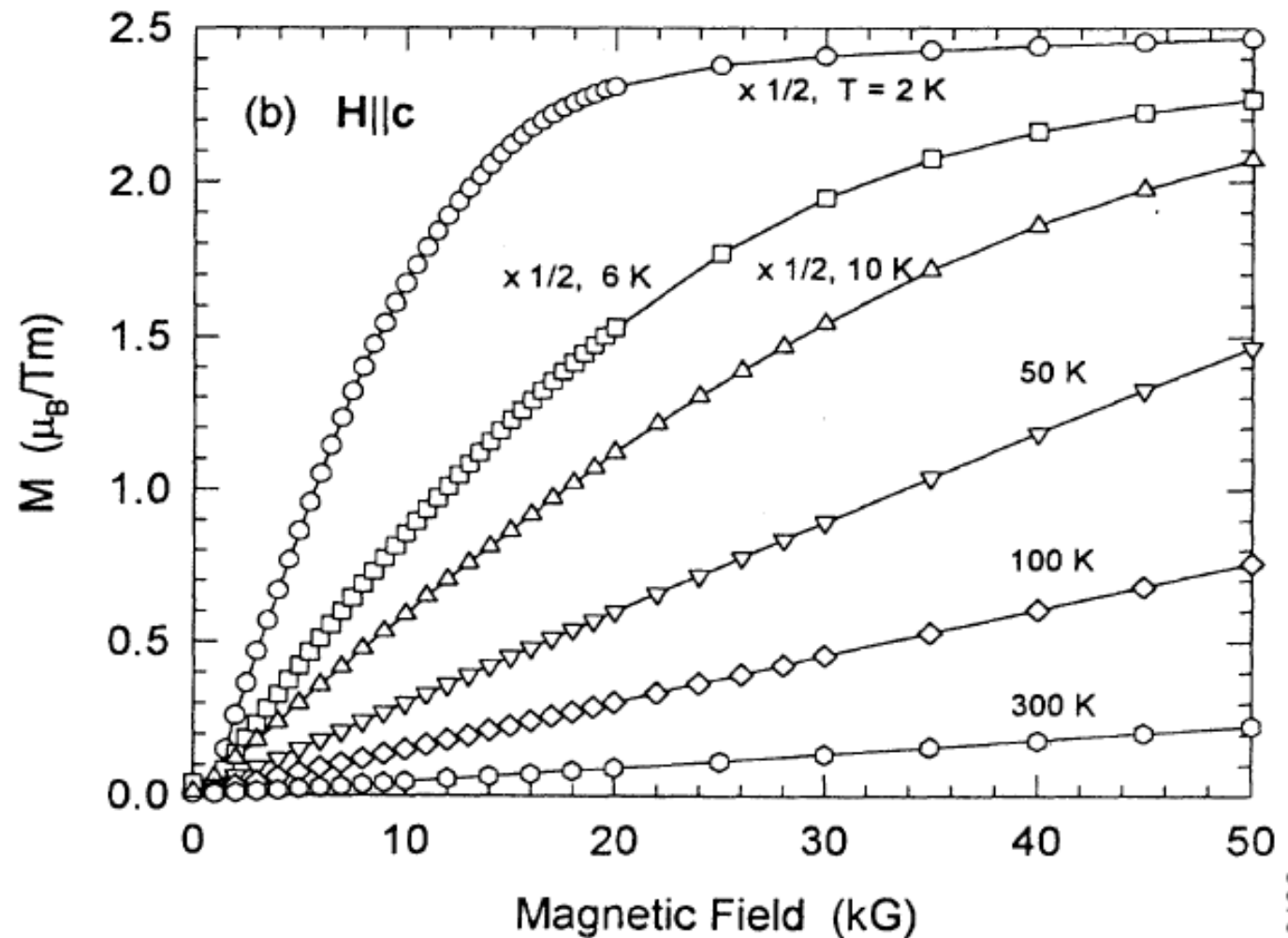


Magnetic susceptibility

For $\mu_B H / k_B T \ll 1$ the magnetization of a paramagnetic, local moment system is linear in H . For such low H , $\chi = M(T) / H$.

Note: gross energy scales: $(1T) * (1\mu_B) \sim (k_B) * (1K)$

Data taken on paramagnetic $TmNi_2B_2C$ (for $T > 10 K$)





Magnetic susceptibility

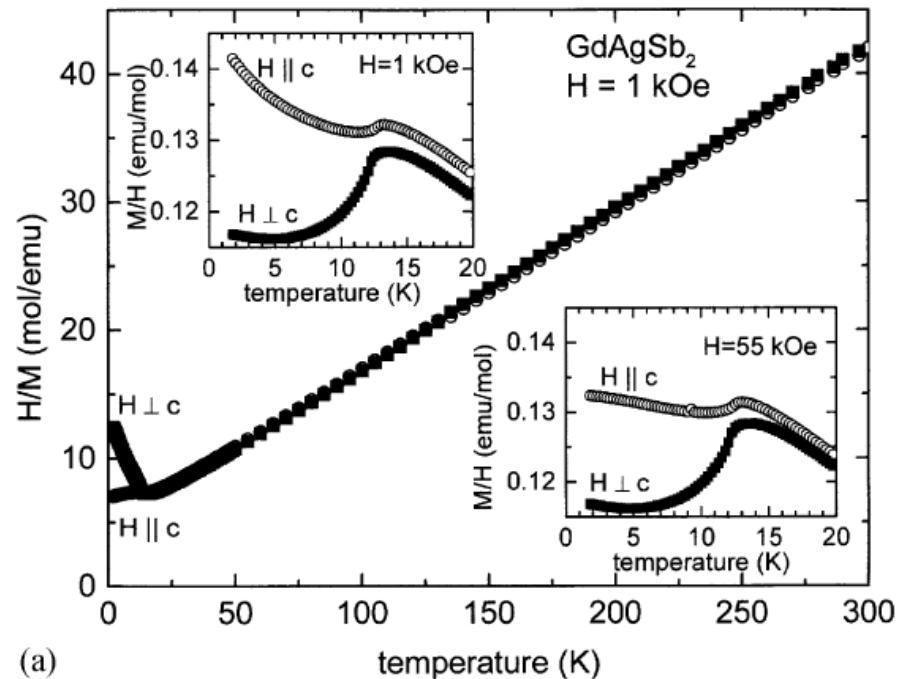
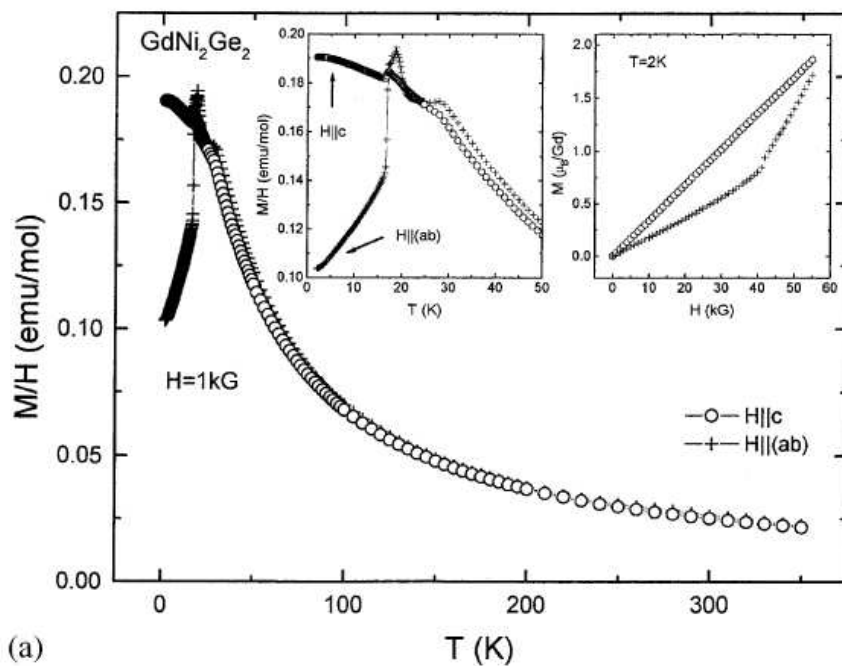
Curie Weiss Law: The temperature dependence of the magnetic susceptibility in the paramagnetic state is given by:

$$\chi = [C/(T - \theta)] + \chi_0$$

$$C = Np_{\text{eff}}^2 \mu_B^2 / 3k_B$$

χ_0 = roughly temperature independent term that is the sum of core diamagnetism, Pauli paramagnetism and Landau diamagnetism

Note: Gd is isotropic since $L = 0$ means no CEF splitting.





Magnetic susceptibility

The rare earth series offers a 14 position knob for tuning magnetism. By controlling S , L , J as well as point symmetry (CEF) we can get a wide variety of magnetic properties: μ_{eff} , μ_{sat} and anisotropy.

f -shell ($l = 3$)								S	$L = \sum l_z $	J		
n	$l_z = 3, 2, 1, 0, -1, -2, -3$											
Ce	1	↓						1/2	3	5/2	} $J = L - S $	$^2F_{5/2}$
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	} $J = L + S$	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



Magnetic susceptibility

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

Kittel, Introduction to Solid State physics 4th edition

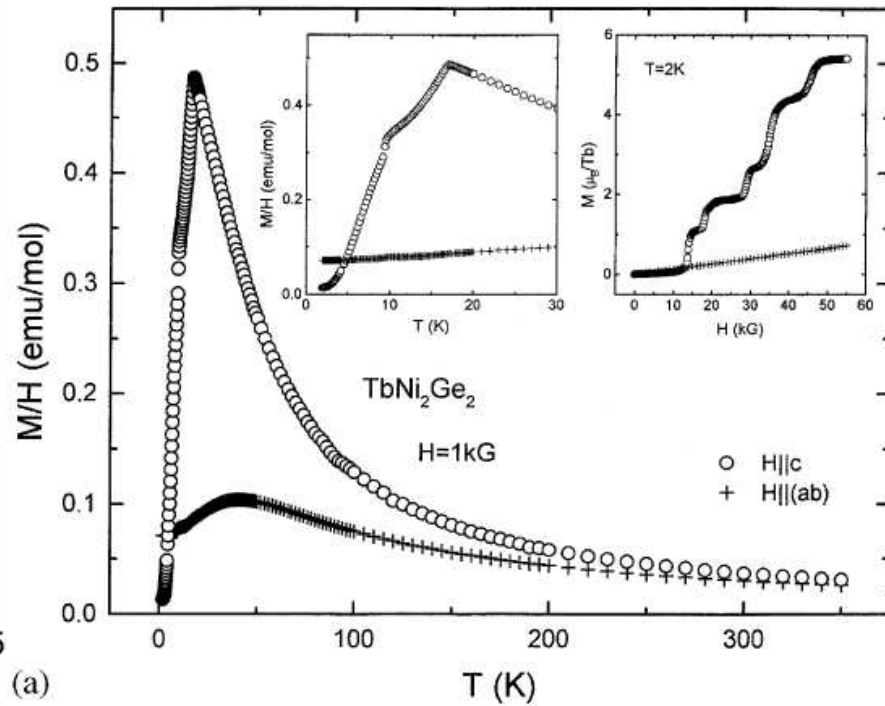
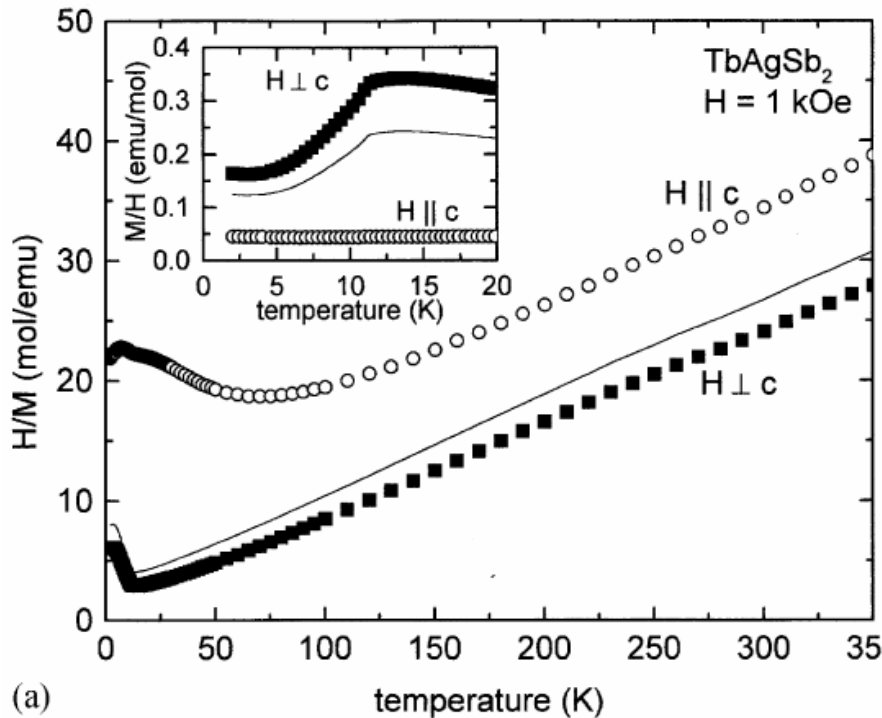
Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J + 1)]^{\frac{1}{2}}$	$p(\text{exp}),$ approximate
Ce ³⁺	4f ¹ 5s ² p ⁶	² F _{5/2}	2.54	2.4
Pr ³⁺	4f ² 5s ² p ⁶	³ H ₄	3.58	3.5
Nd ³⁺	4f ³ 5s ² p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² p ⁶	⁵ I ₄	2.68	—
Sm ³⁺	4f ⁵ 5s ² p ⁶	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	4f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



Magnetic susceptibility

For R with finite L (i.e not Gd^{3+} or Eu^{2+}) there will be CEF splitting that can give rise to significant anisotropy. The degree of anisotropy will depend on the R as well as the point symmetry it is in.

This anisotropy can be clearly seen in χ^{-1} as well as χ plots.

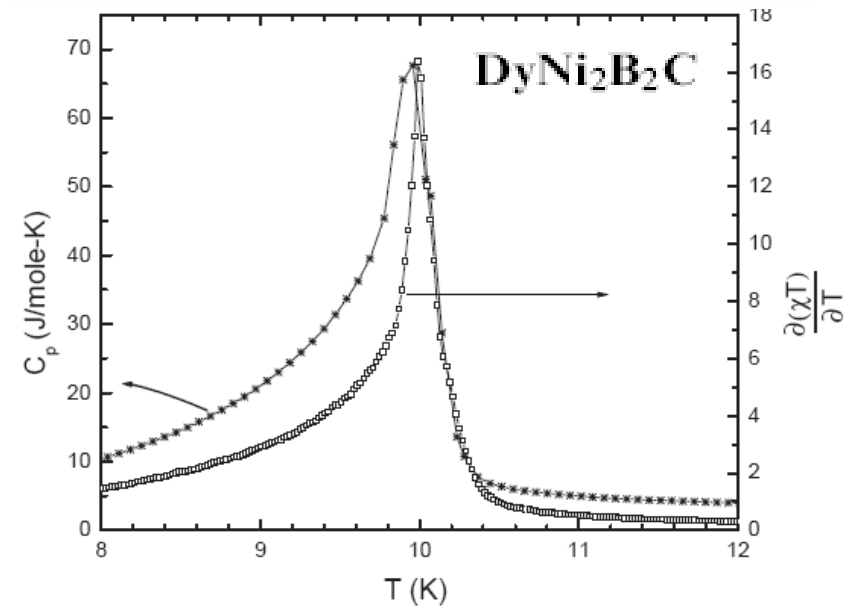
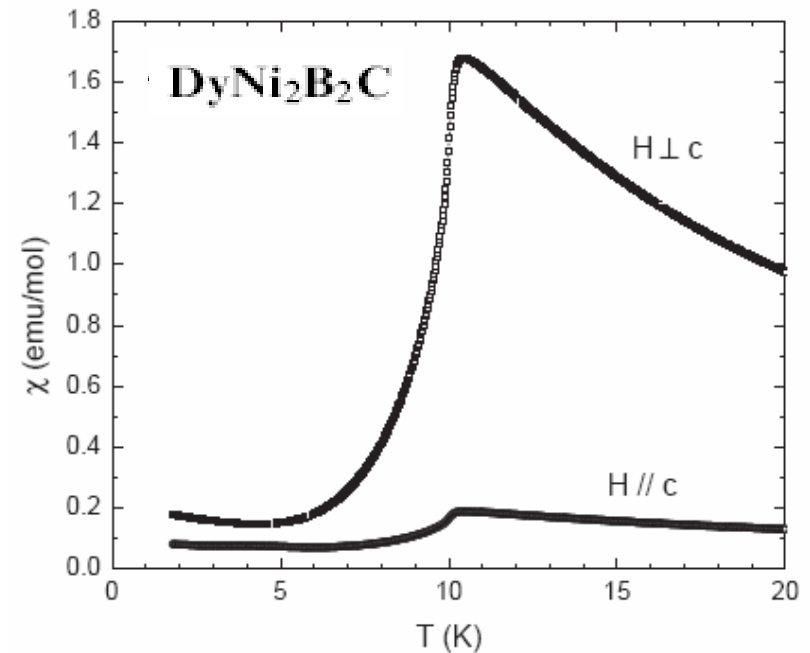




Magnetic susceptibility

In addition allowing for evaluation of p_{eff} and θ the magnetic susceptibility can be used to determine the antiferromagnetic ordering temperature, T_N . Although it is tempting to simply take the temperature of the maximum χ value, this only gives a rough estimate. Near T_N , $d(\chi T)/dT$ has the same temperature dependence as C_p , so the temperature of the maximum in $d(\chi T)/dT$ is considered a more reliable criterion for determination of T_N .

M. Fisher, Philos. Mag. 7 (1962) 1731.

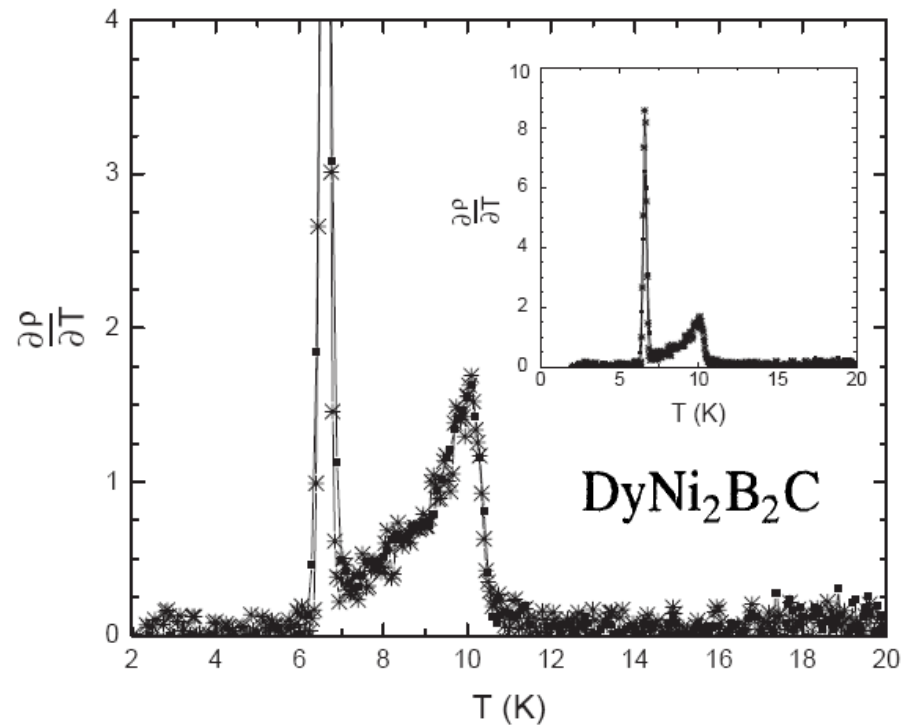
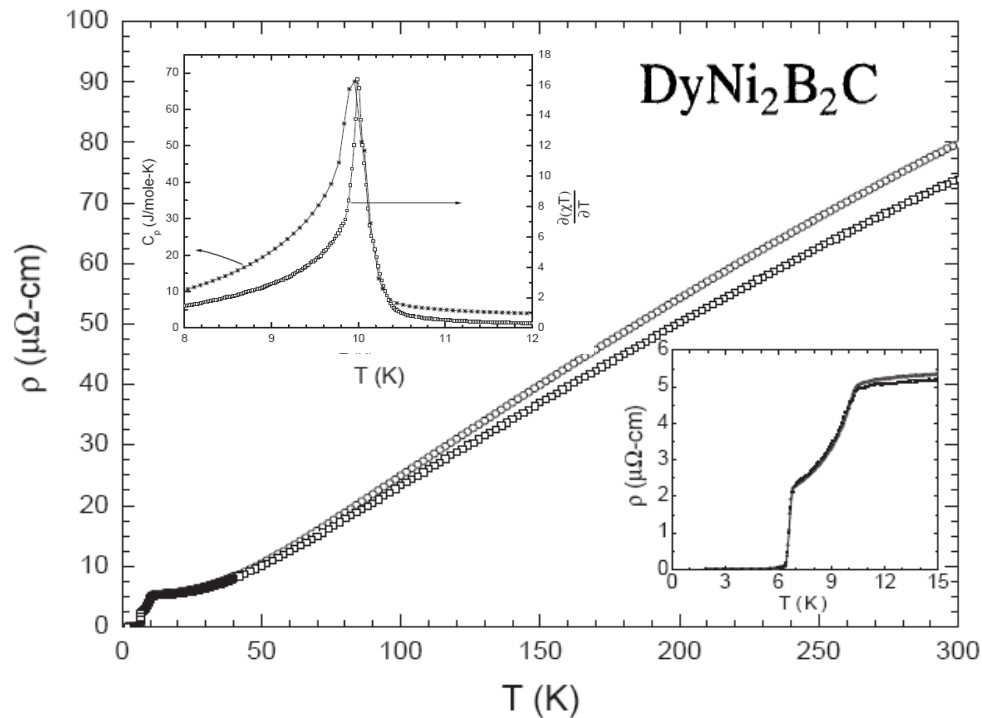




A detour back to resistivity for a moment

$d\rho/dT$ can also show similar temperature dependencies near T_N , but only for a limited number of transitions. In general though, $d\rho/dT$ can be used as a criterion for T_N or T_C , but this will depend on the noise level of the data.

M. E. Fisher, J. S. Langer, *Philos. Mag.*, 7 (1962) 1731.





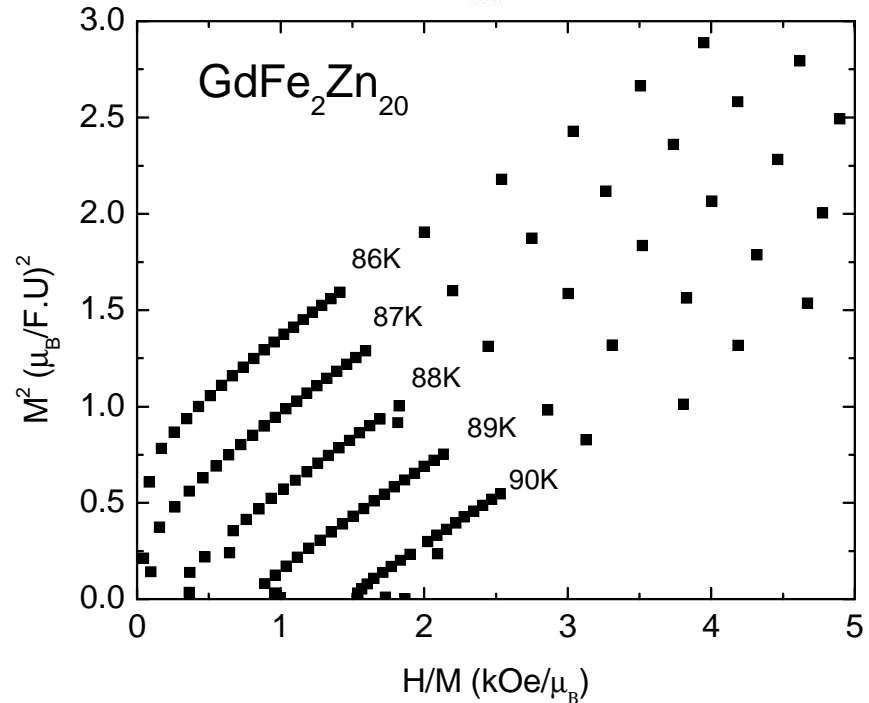
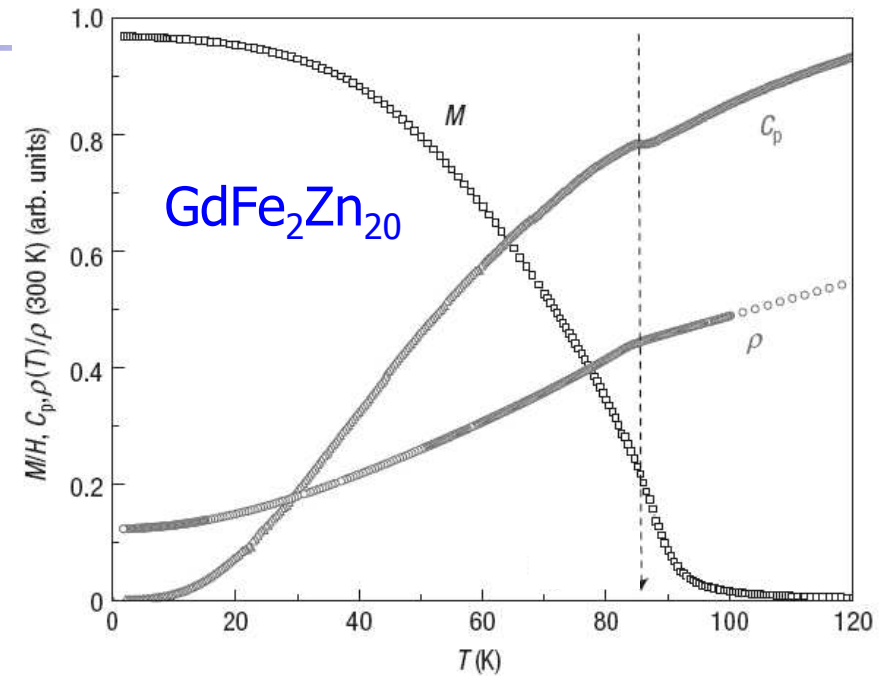
Magnetic susceptibility

Ferromagnetic transitions

The transition to the ferromagnetic state is conspicuous, but the actual T_C value is hard to extract from the $M(T)$ data. (It can actually be much clearer in the $C_p(T)$ or $\rho(T)$ data.)

One way of estimating T_C from magnetization data is to plot $M(H)$ isotherms as an "Arrot Plot": M^2 vs. H/M . The data linearly go through the origin when $T \sim T_C$.

Grossly this is similar to seeing when a spontaneous magnetization appears in low field.





Magnetic susceptibility

Using susceptibility, detailed information about R-series can be determined. This information, combined with resistivity and specific heat data can often provide enough insight for choosing samples for specific purposes (Ising spin-glass, metamagnetism, etc.).

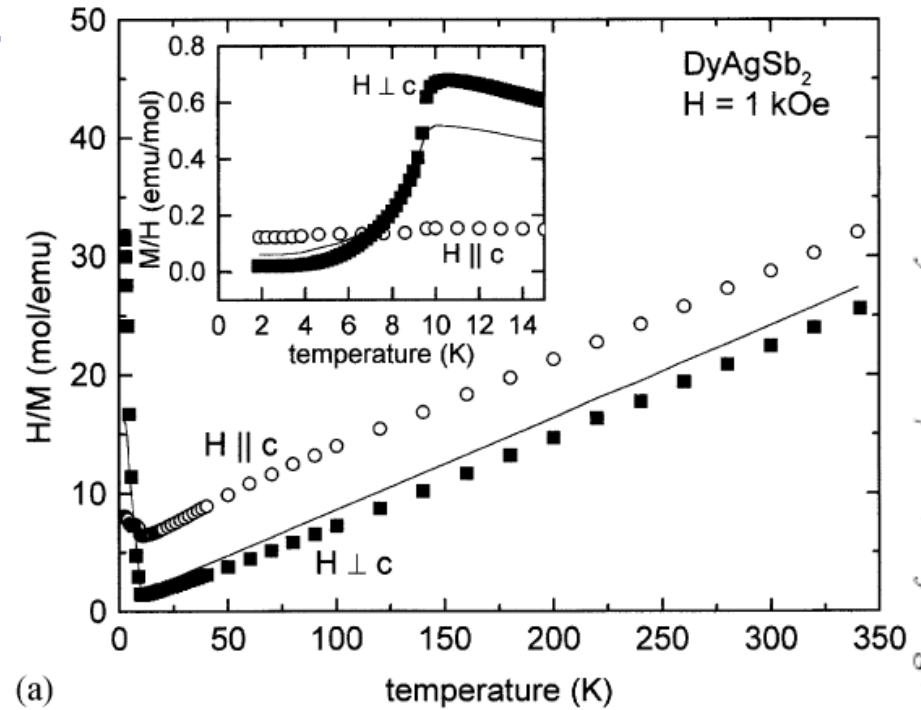


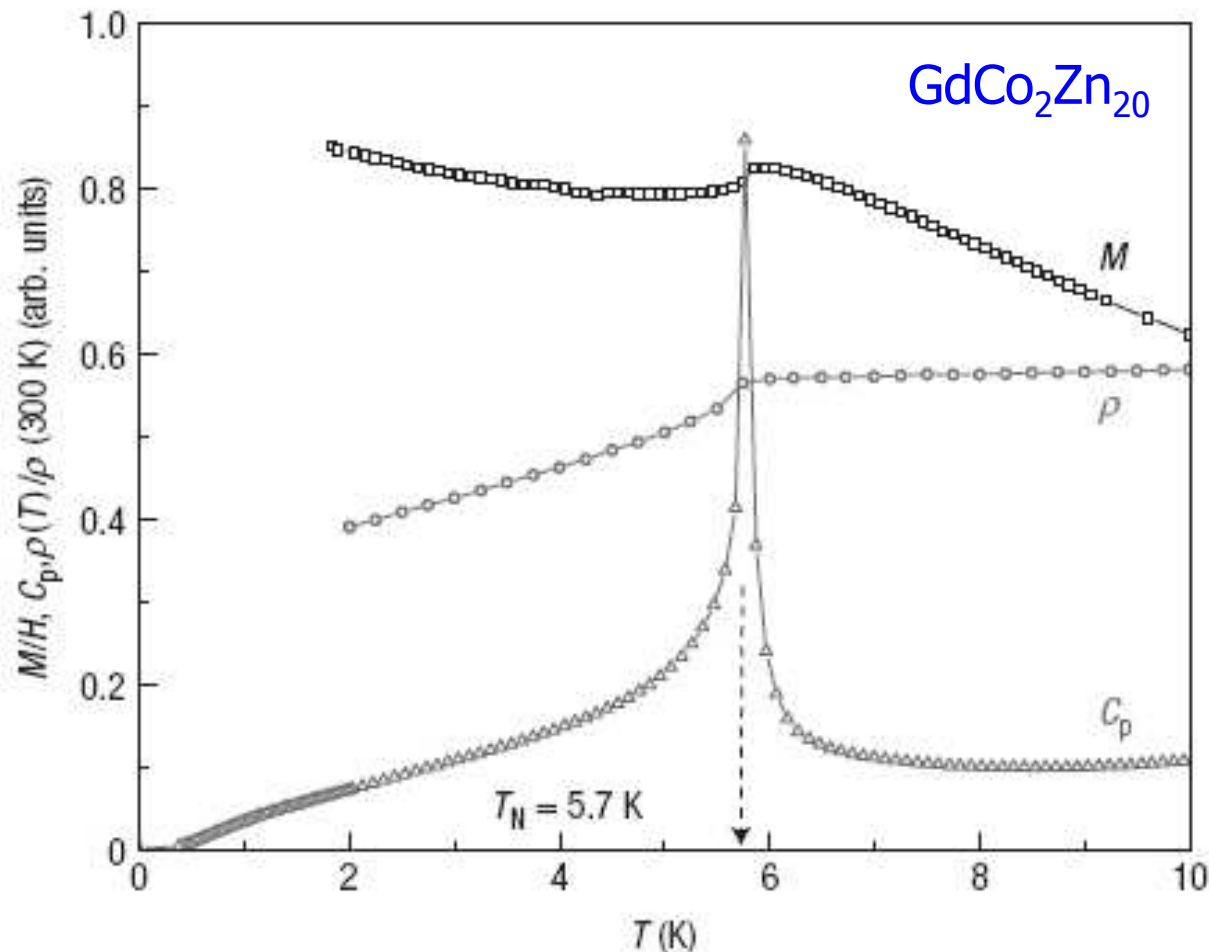
Table 2

Magnetic properties of the RAgSb₂ compounds. Uncertainties reflect experimental limits and in the case of T_M include any variation between magnetic susceptibility and resistivity data. Crystalline electric field parameters (α_J , $\langle r^2 \rangle$) are from Ref. [29]

Compound	T_M (K) (± 0.1 K)	μ_{eff} (μ_B) (± 0.1 K)	θ_{ave} (K) (± 0.2 K)	θ_c (K) (± 0.2 K)	θ_{ab} (K) (± 0.2 K)	B_2^0 (K) (± 0.3 K)	$\langle r^2 \rangle (a_0^2)$	$\alpha_J \times 10^2$	A_2^0 (± 0.3)
CeAgSb ₂	9.6	2.3	16.8	-27.9	34.6	6.5	1.200	-5.71	-1.0
PrAgSb ₂	2.8	3.6	-7.2	-48.5	-6.3	1.8	1.086	-1.05	-1.6
NdAgSb ₂	2.9	3.6	-14.2	-45.3	-4.0	1.4	1.001	-0.643	-2.2
SmAgSb ₂	8.7	—	—	—	—	—	0.883	4.13	—
GdAgSb ₂	12.8	7.9	-32.0	-32.0	-32.0	—	—	—	—
TbAgSb ₂	11.0	10.2	-41.4	-125	-19.0	2.1	0.758	-1.01	-2.8
DyAgSb ₂	9.4	10.3	-10.1	-86.3	7.1	1.2	0.726	-0.635	-2.7
HoAgSb ₂	5.4	10.1	-1.7	-39.5	9.2	0.6	0.695	-0.222	-3.7
ErAgSb ₂	3.8	9.1	-2.2	9.8	-14.6	-0.3	0.666	0.254	-1.9
TmAgSb ₂	~ 1.8	6.6	0.9 ± 0.5	53 ± 0.5	-44 ± 0.5	-1.9 ± 0.7	0.640	1.01	-3.0 ± 0.7



We have now seen how $\rho(T)$, $C_p(T)$, and $\chi(T)$ can be used to determine magnetic ordering temperatures (as well as many other useful parameters).



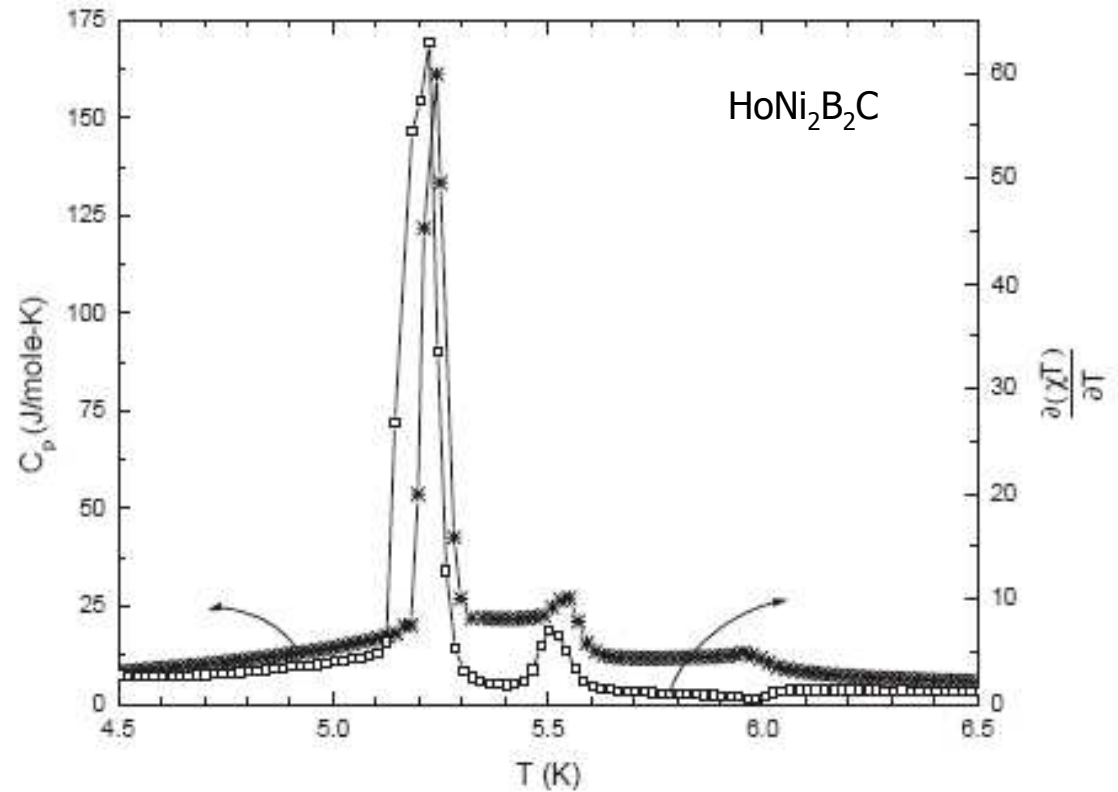
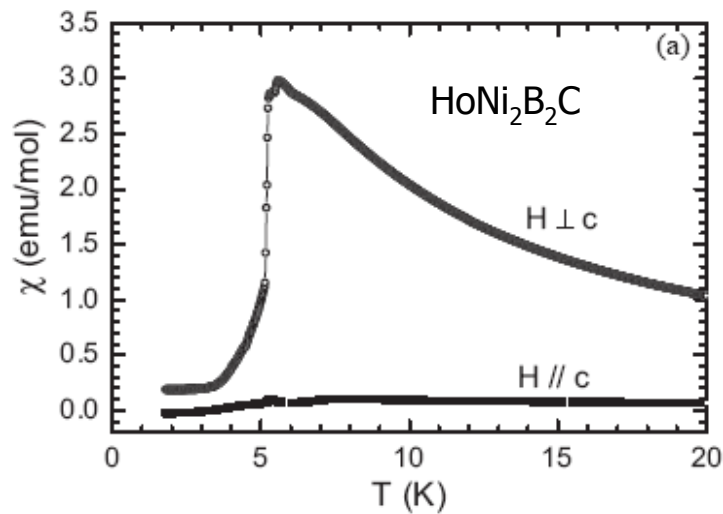
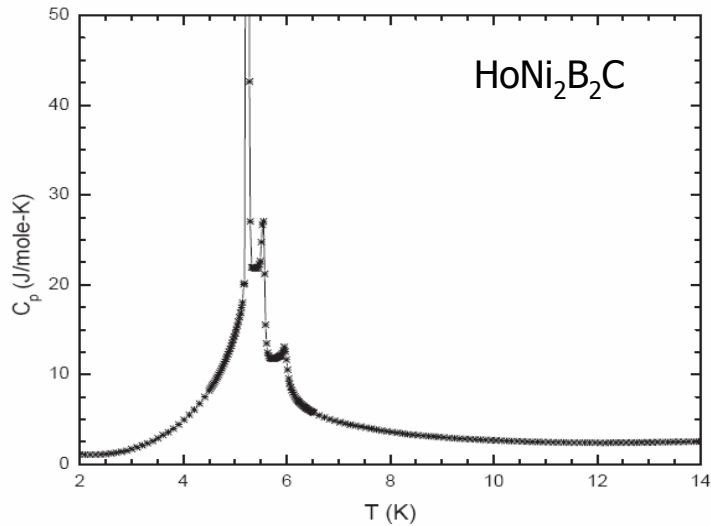
respectively. **b**, GdCo₂Zn₂₀; the full scale represents 1.4 e.m.u. mol⁻¹, 50 J mol⁻¹ K⁻¹ and 0.20 for M/H , C_p and $\rho(T)/\rho(300\text{ K})$, respectively. For GdFe₂Zn₂₀, $\rho(300\text{ K}) = 73\ \mu\Omega\text{ cm}$ and for GdCo₂Zn₂₀, $\rho(300\text{ K}) = 60\ \mu\Omega\text{ cm}$.

What about multiple transitions?



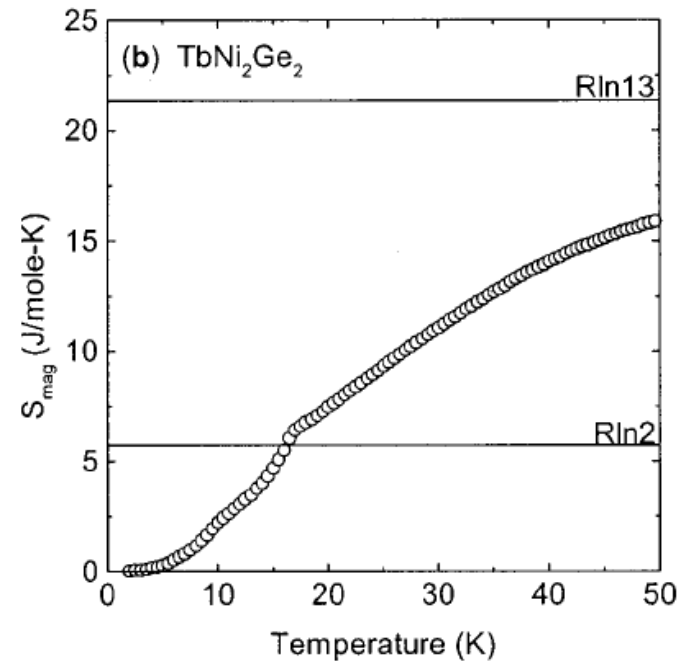
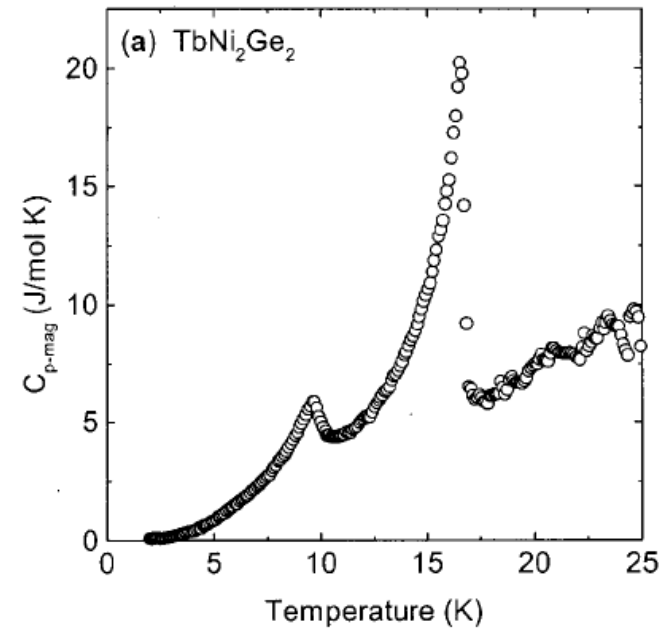
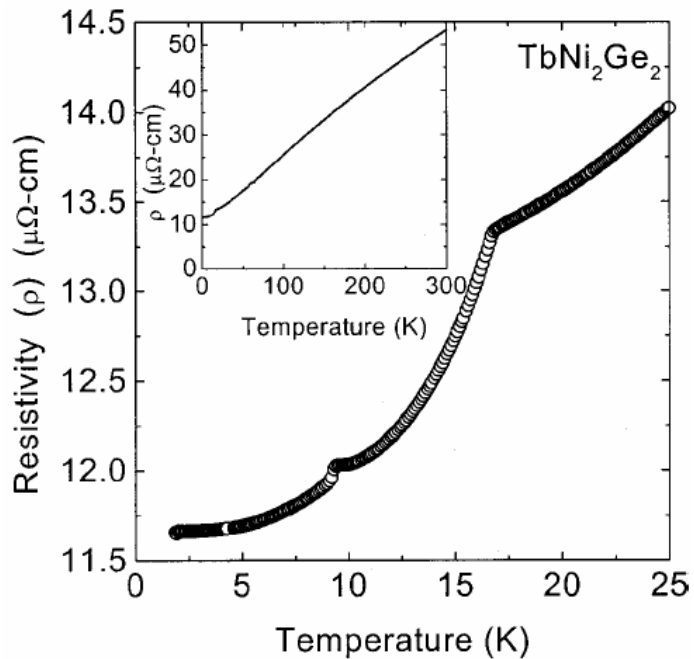
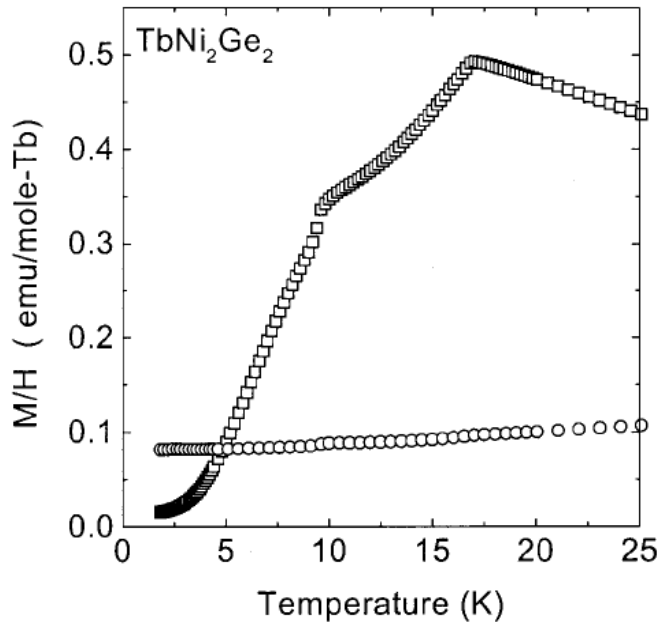
Multiple transition temperatures

HoNi₂B₂C has a cascade of magnetic transitions (AF) between 6 and 5 K. They are clear in both C_p and χ data.



Multiple transitions in temperature and field

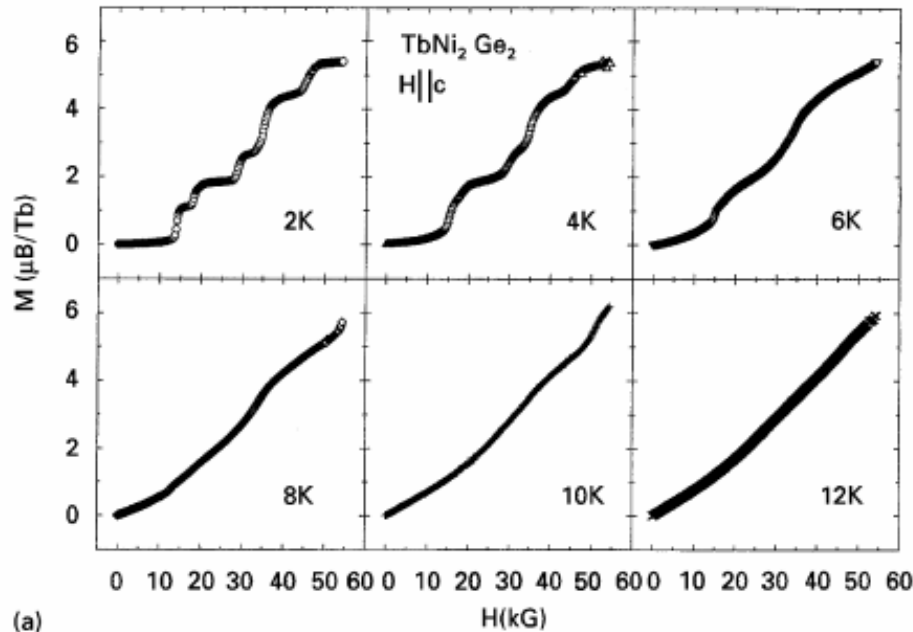
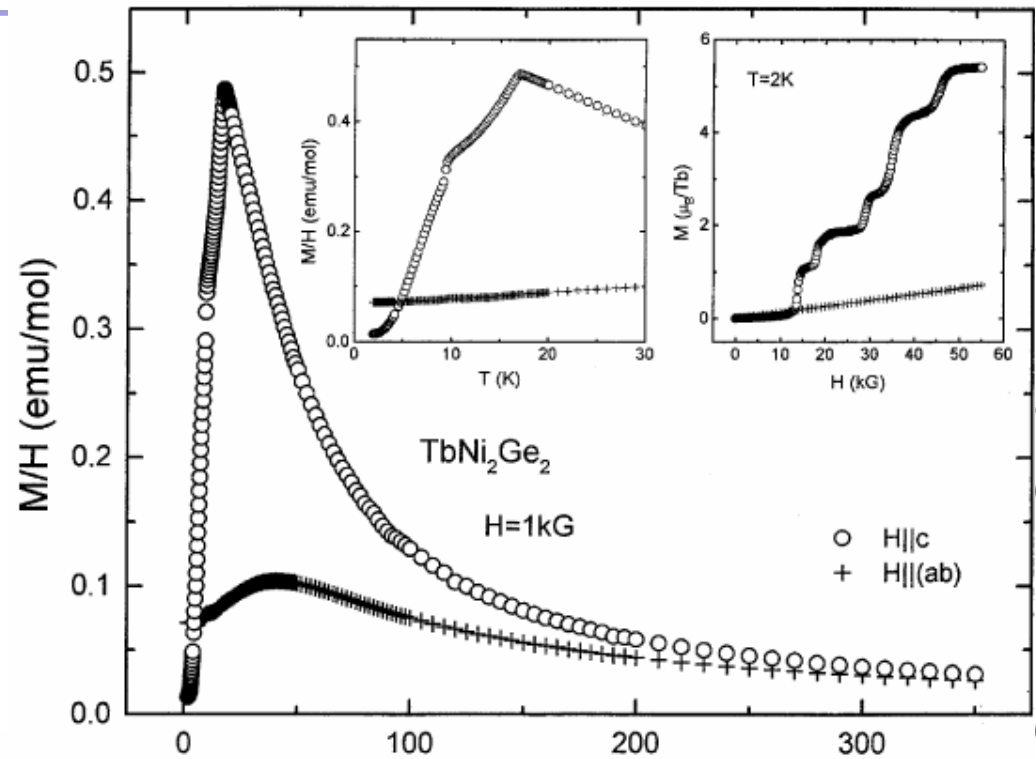
TbNi₂Ge₂ has
two clear
transitions in
zero (low) field



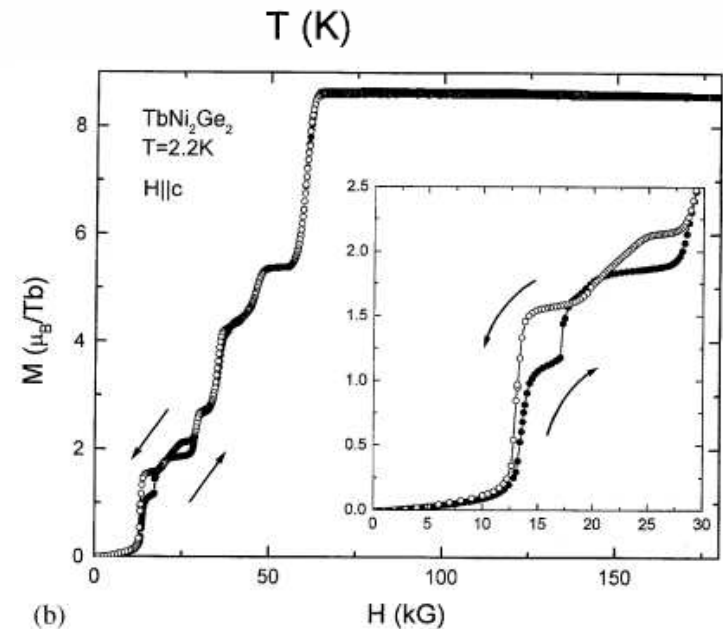


Multiple transitions in temperature and field

When a magnetic field is applied along the c-axis for $T < T_N$ there are a cascade of meta-magnetic (field stabilized) phase transitions.



(a)

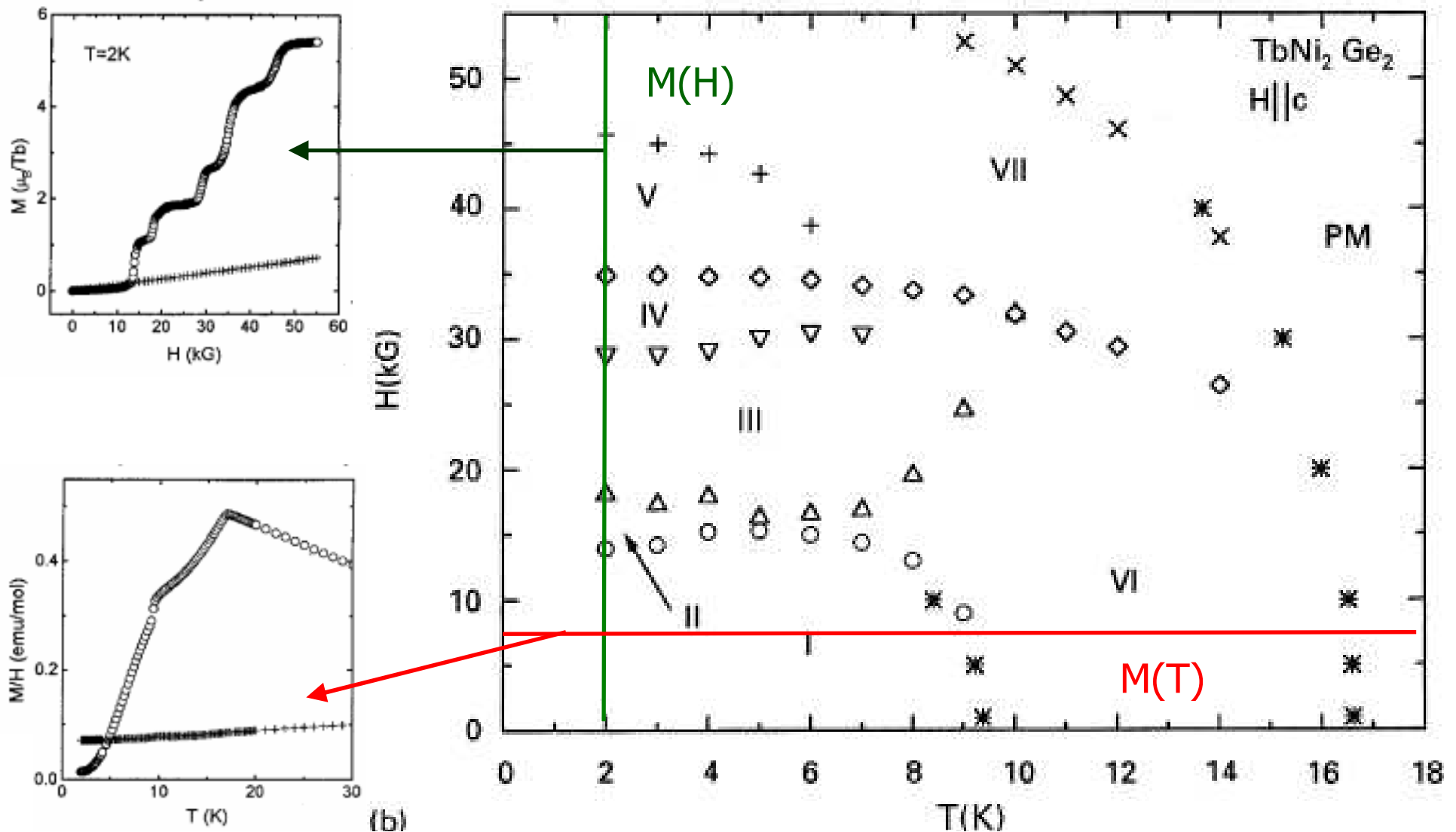


(b)



Multiple transitions in temperature and field

$M(H)$ and $M(T)$ data can be used to construct a H-T phase diagram that delineates regions of differing magnetic order.

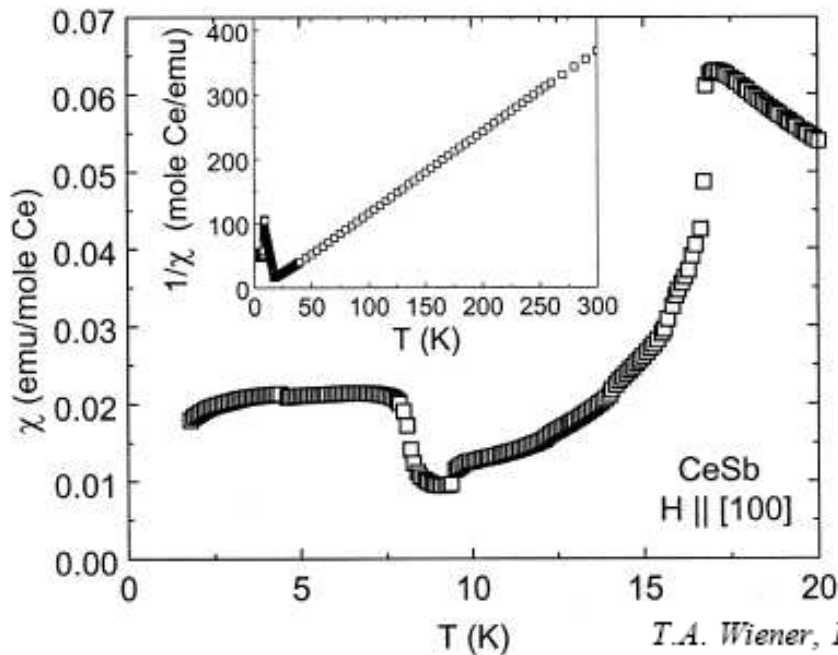
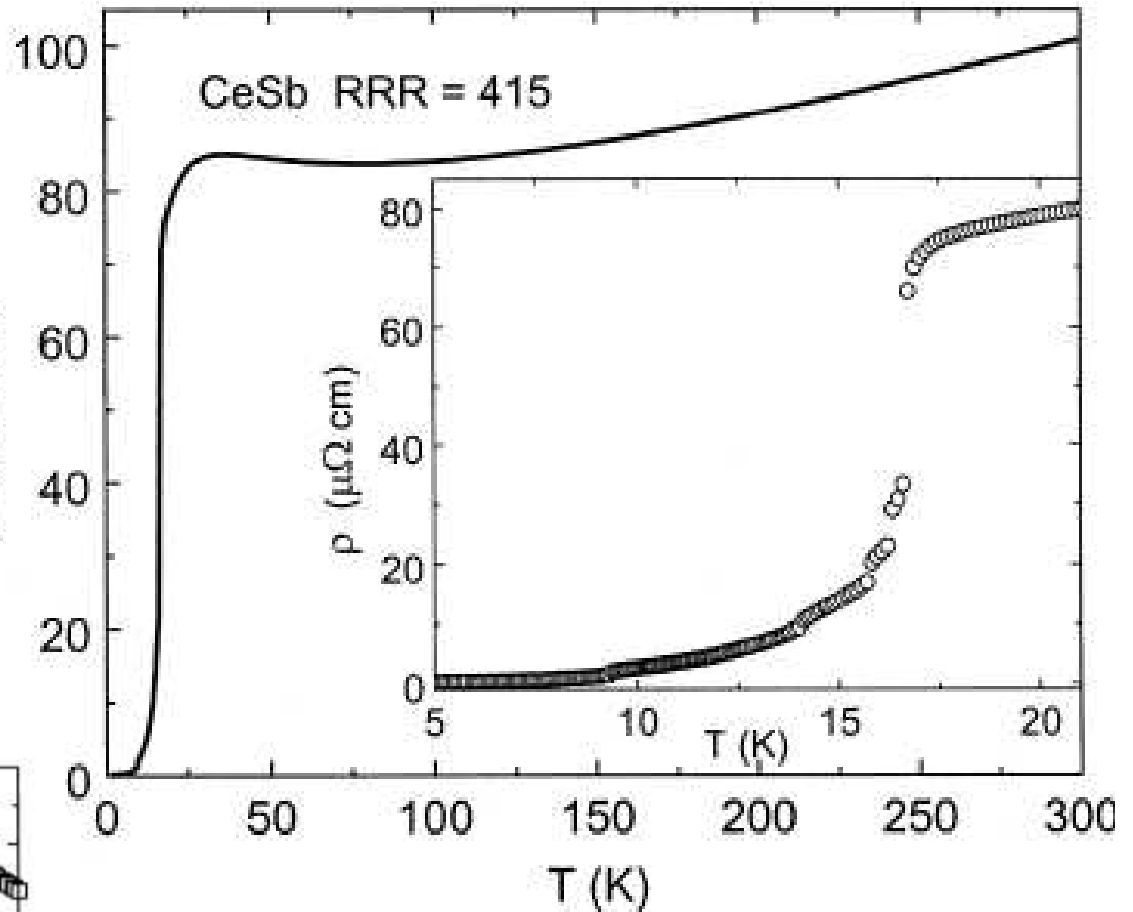




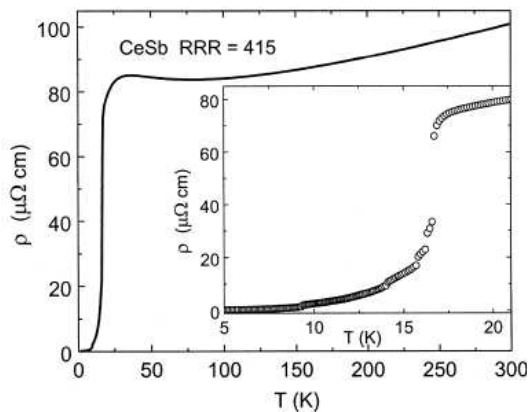
Multiple transitions in temperature and field

CeSb

CeSb can be grown in exquisite purity from Sn flux. At first glance ρ and χ data seem to be a bit noisy at low T....

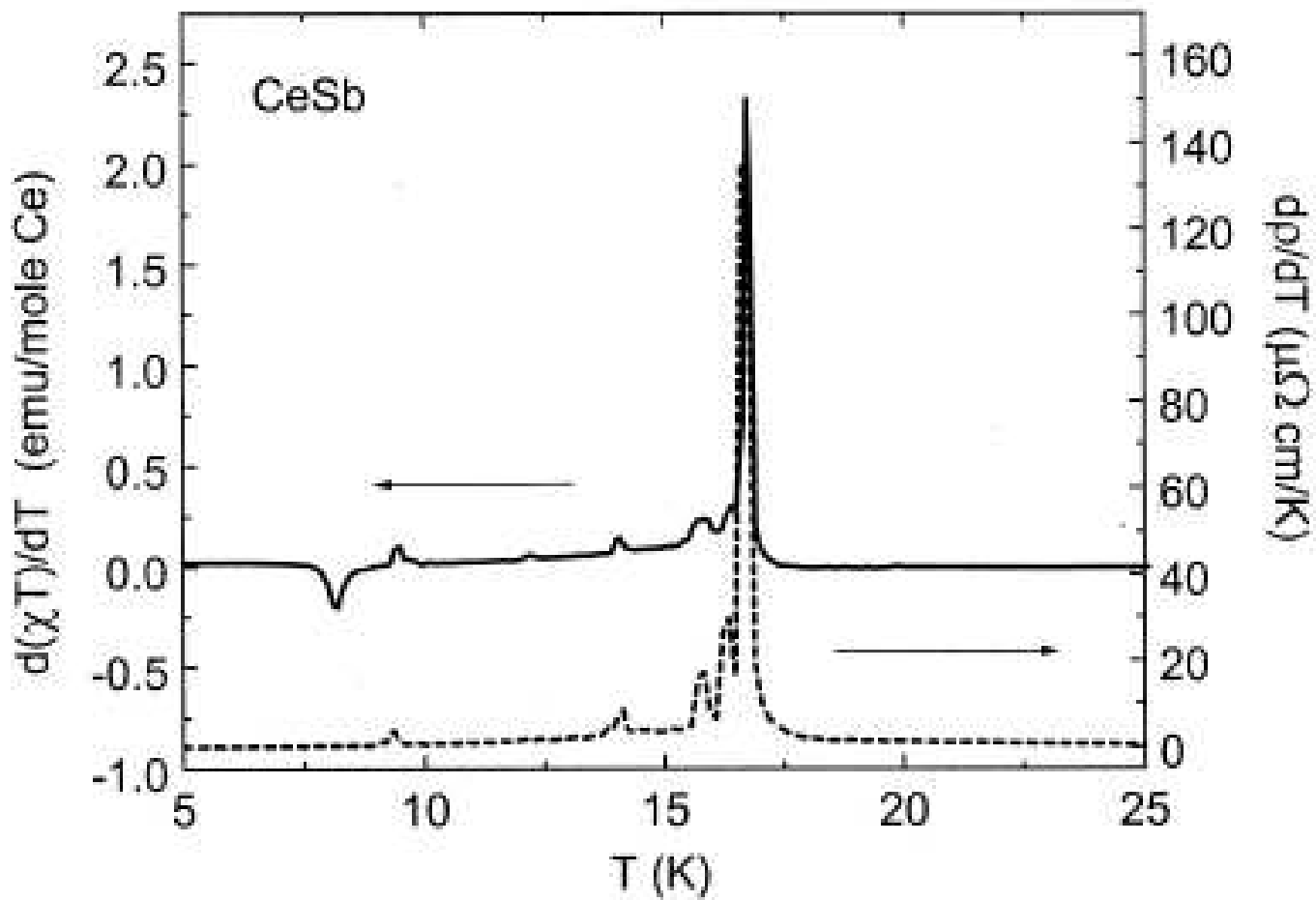
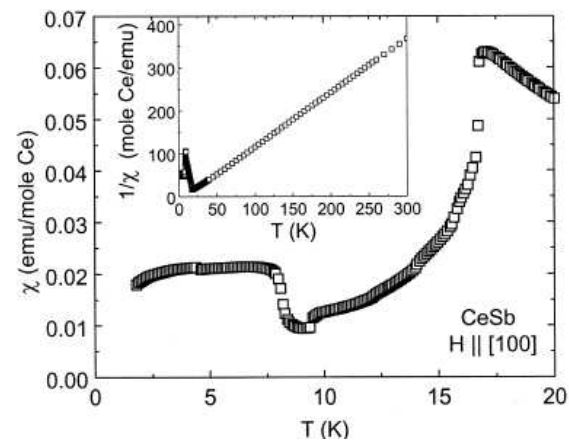


Actually CeSb has a formidable number of phase transition in zero and applied field and excellent (Sn flux grown) crystals allow us to examine them in detail.



CeSb

Both χ and ρ data reveal a multitude of transitions.





Multiple transitions in temperature and field

CeSb

These multiple transition appear in finite field as well.

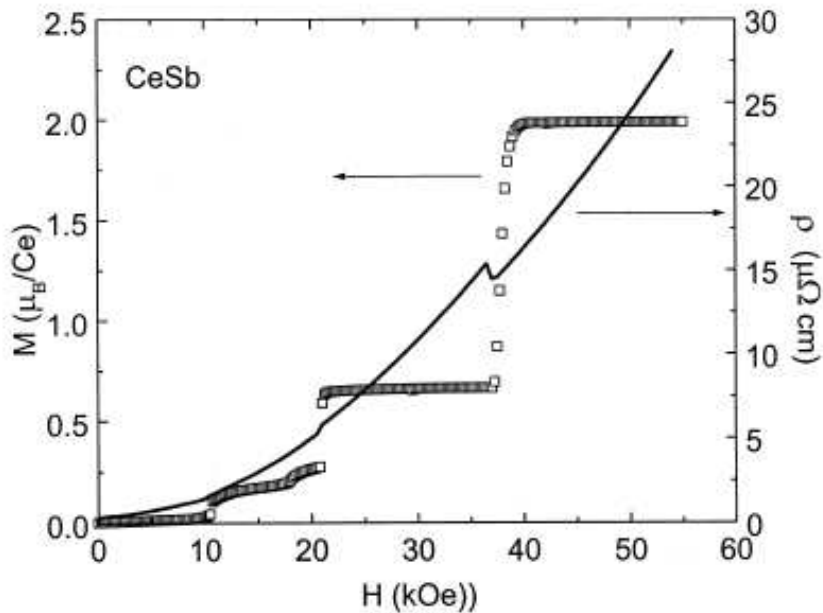


Fig. 4. Magnetization as a function of applied field (\square , left-hand axis) and resistivity as a function of applied field (—, right-hand axis) at 5 K.

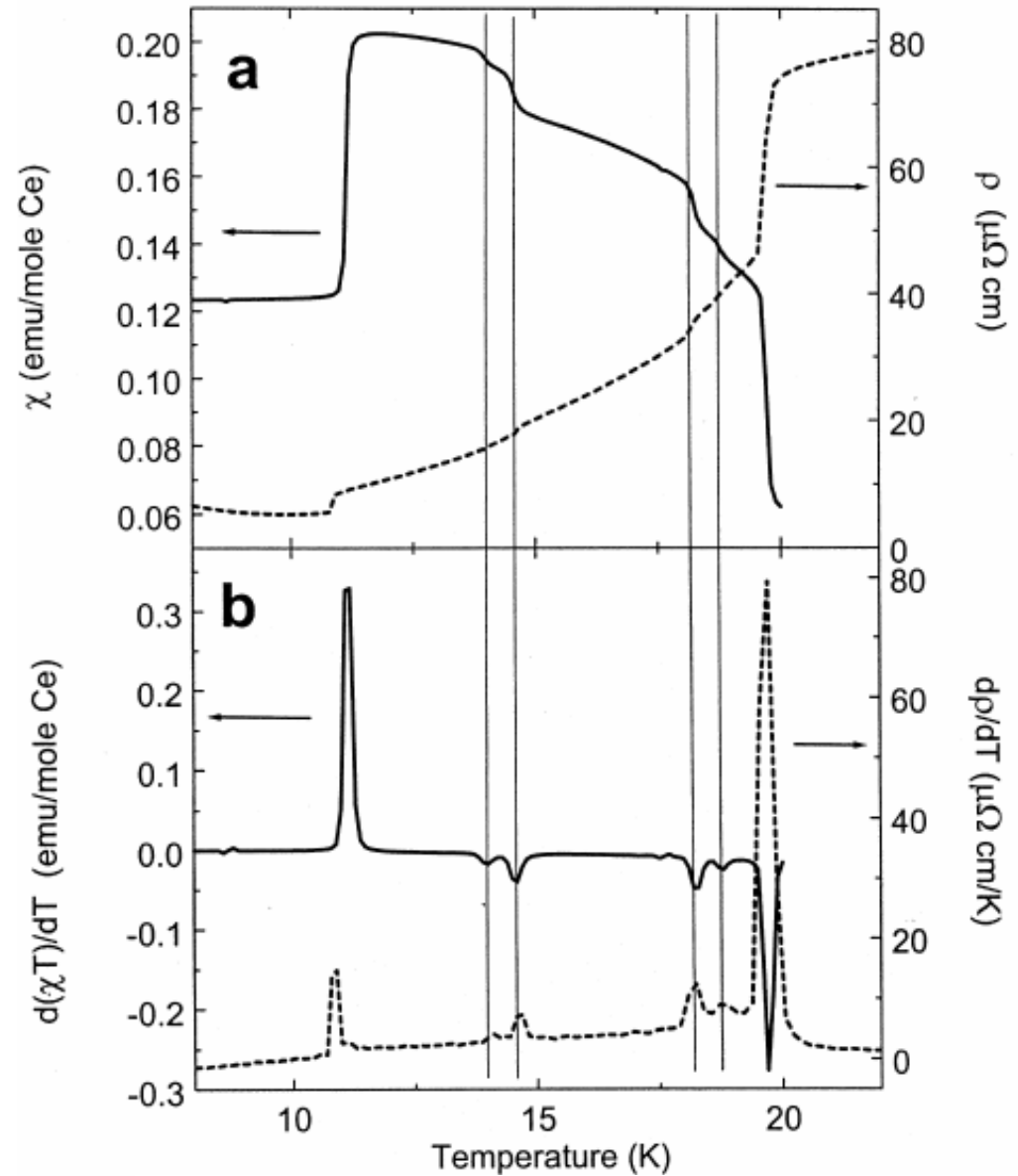


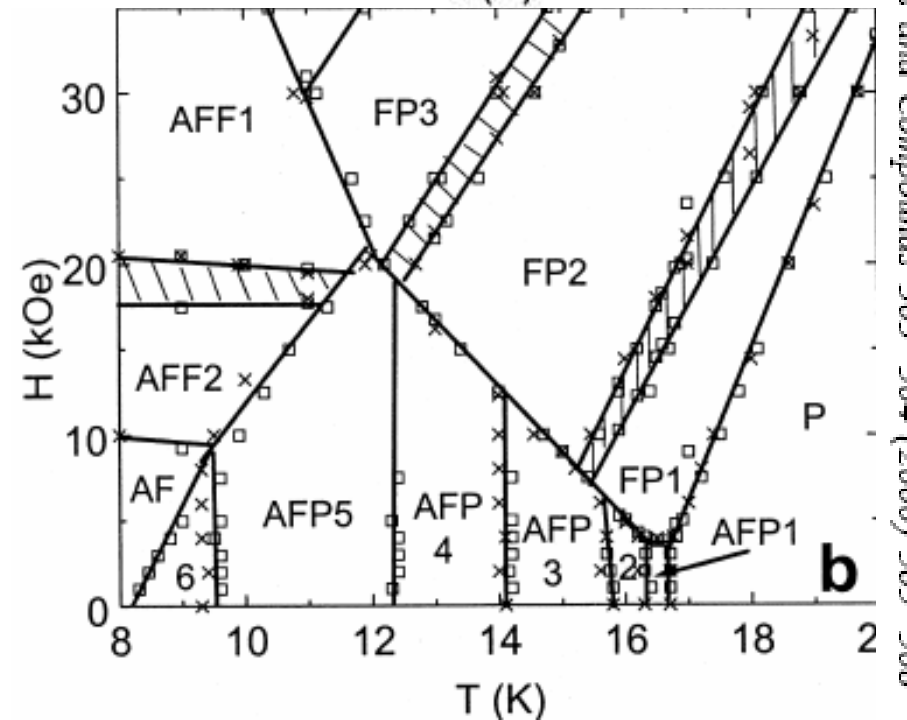
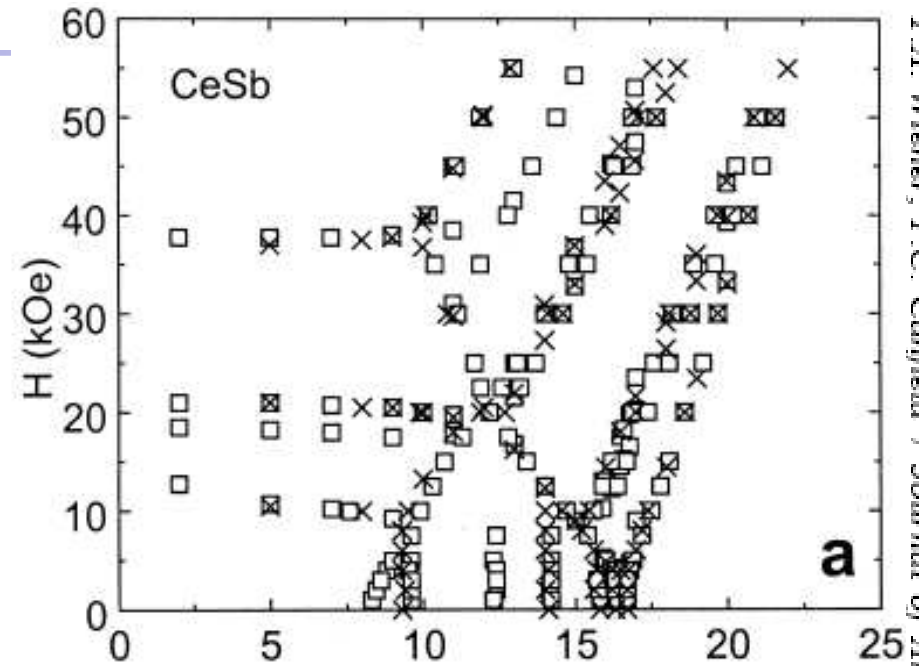
Fig. 6. (a) Dc susceptibility (—, left-hand axis) and resistivity (---, left-hand axis) as a function of temperature at 30 kOe. (b) $d(\chi T)/dT$ (—, left-hand axis) and $d\rho/dT$ (---, right-hand axis) at 30 kOe as a function of temperature. In both panels, vertical arrows highlight the boundaries of proposed new phases as described in text.



Multiple transitions in temperature and field

CeSb

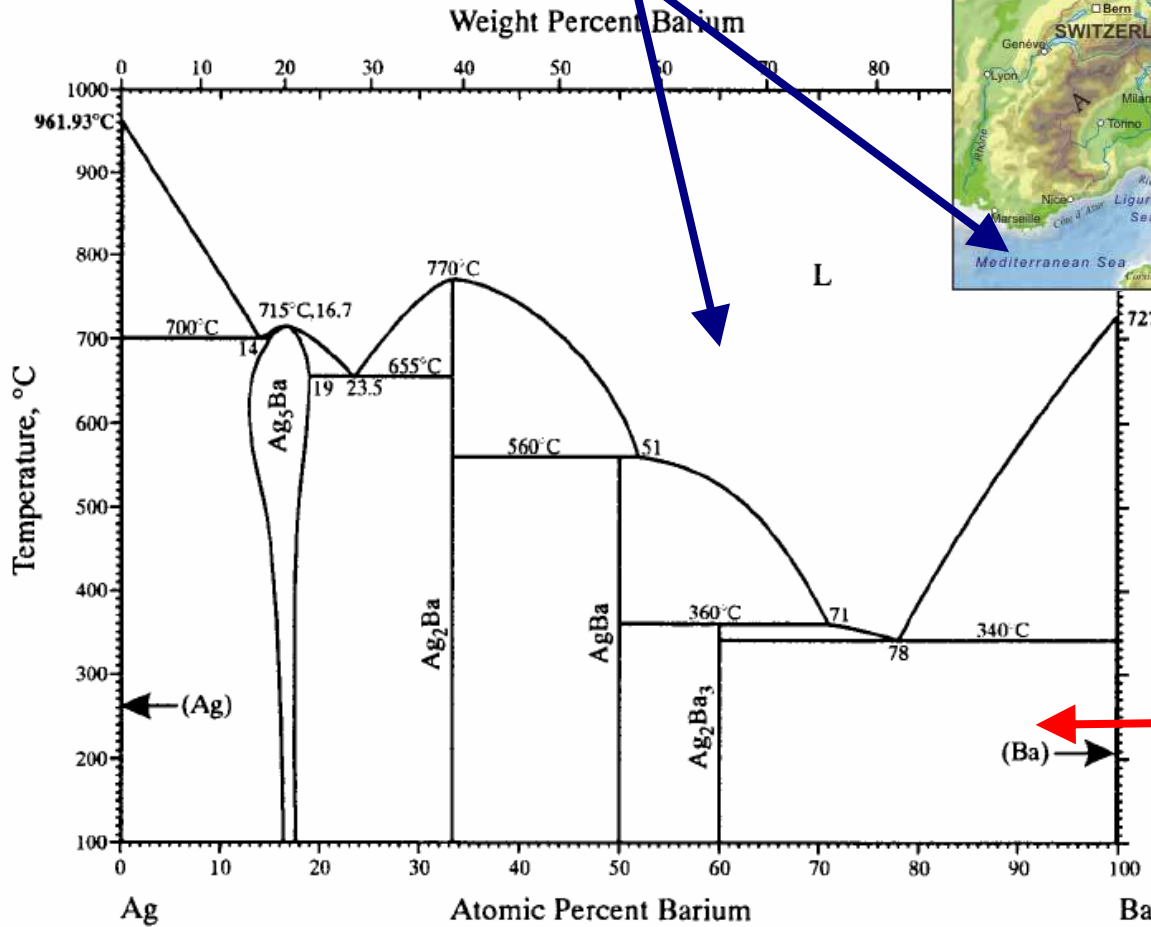
$M(H)$, $M(T)$, $\rho(H)$ and $\rho(T)$ data can be used to assemble an H-T phase diagram of fantastic detail. This system was studied extensively in the 70's and 80's by several neutron scattering groups as well as serving as the inspiration for the ANNNI model. The precise origin of this complexity is still an open question.





We have now seen several other types of phase diagrams. Not mapping out liquid and solid,

Liquids

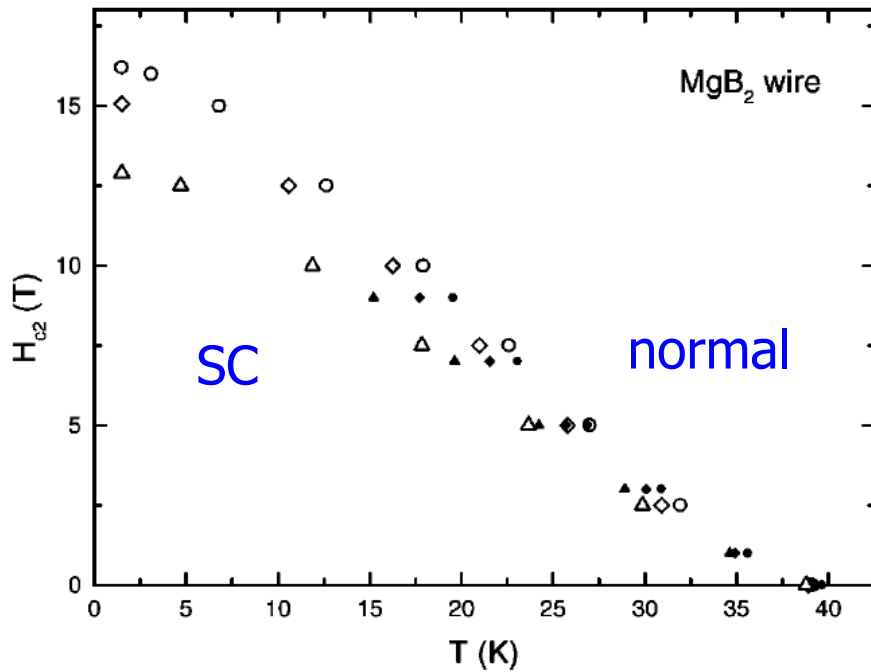


Solids

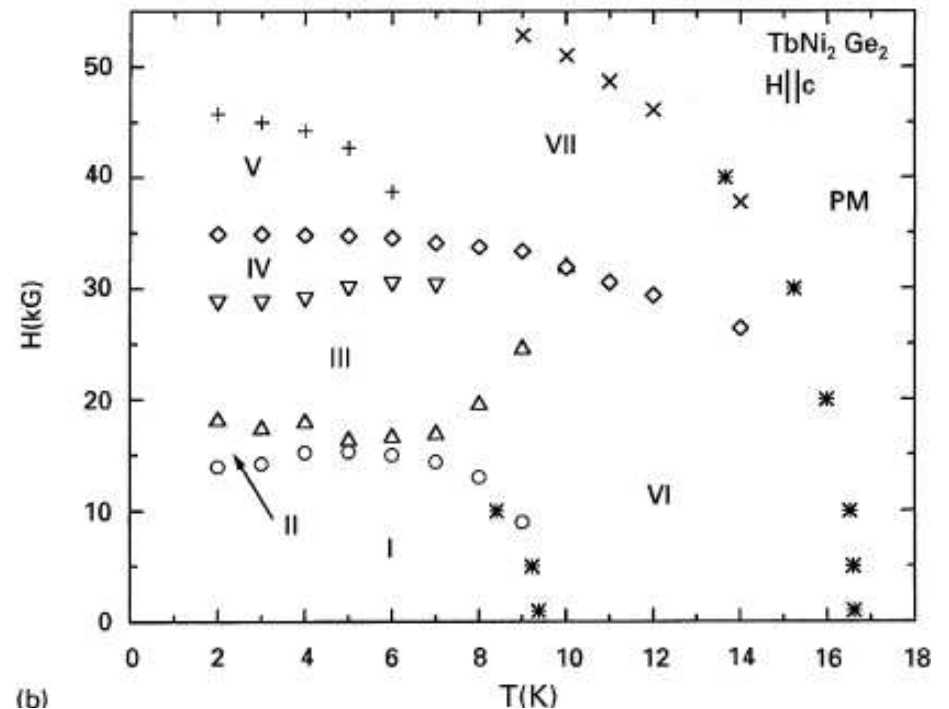
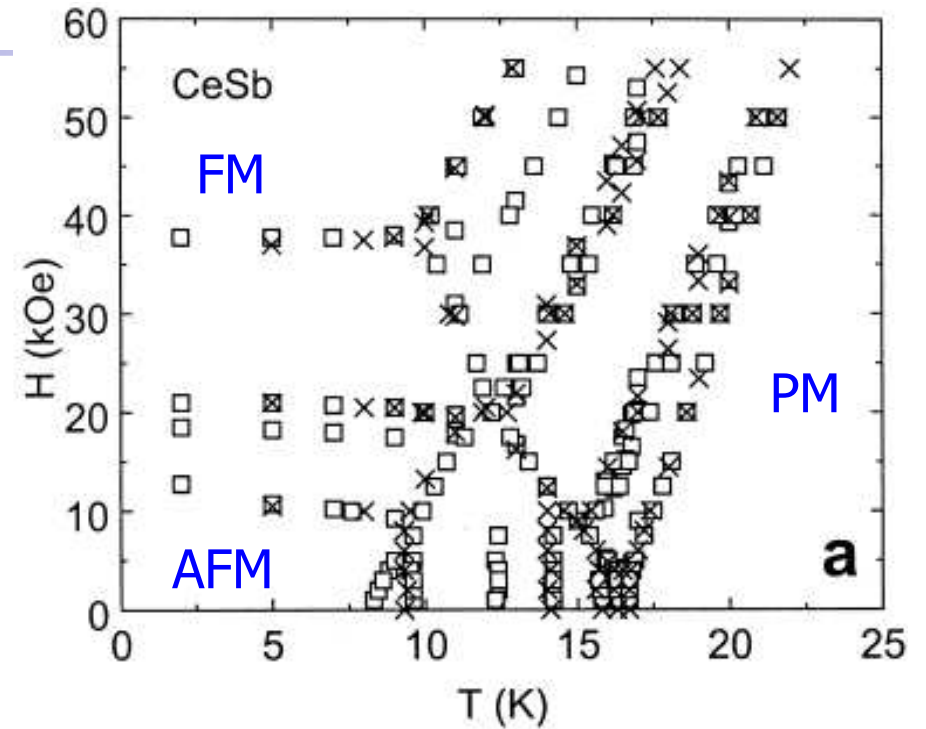
but instead,



mapping out the
electronic / magnetic
phases.



Phase diagrams can involve more than applied field and temperature (or composition and temperature).

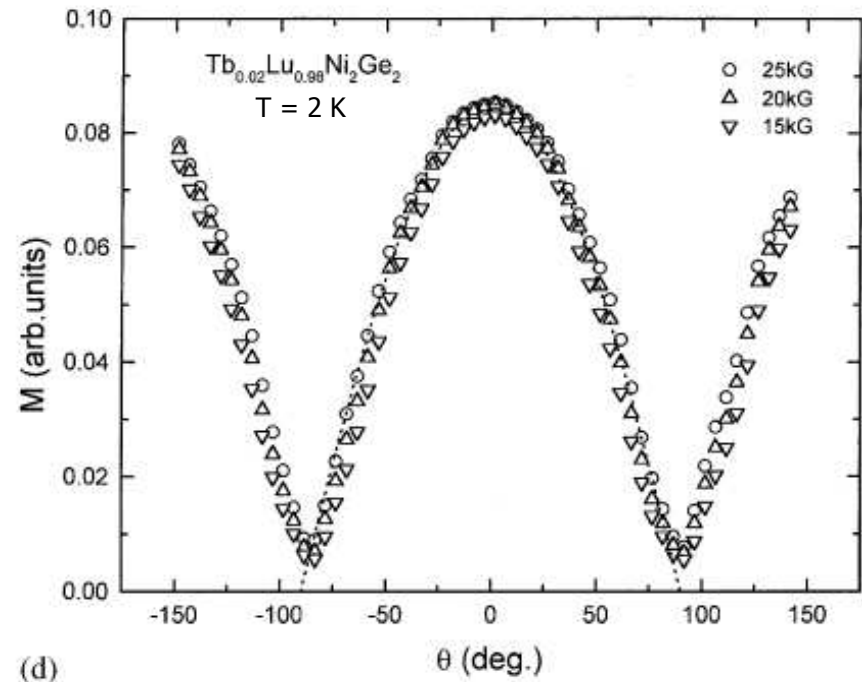
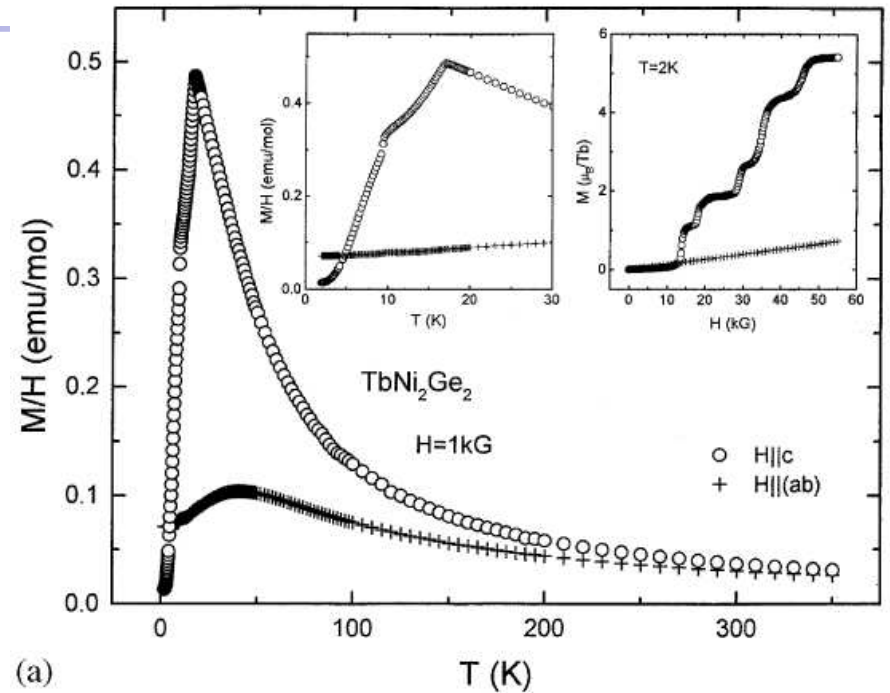




Angular dependent effects

Recall that we found TbNi_2Ge_2 to be quite anisotropic, but the magnetic ordering helps to obscure just how anisotropic the local moments really are.

By diluting Tb into the non-magnetic LuNi_2Ge_2 we can see just how anisotropic the low T magnetization is in the paramagnetic state. The local Tb moments are extremely axial and their longitudinal magnetization is simply their projection along the field direction: $M(\theta) = M_0 \cos(\theta)$. This makes TbNi_2Ge_2 a model, Ising system, i.e. the moment is either spin up or spin down along the Ising axis.

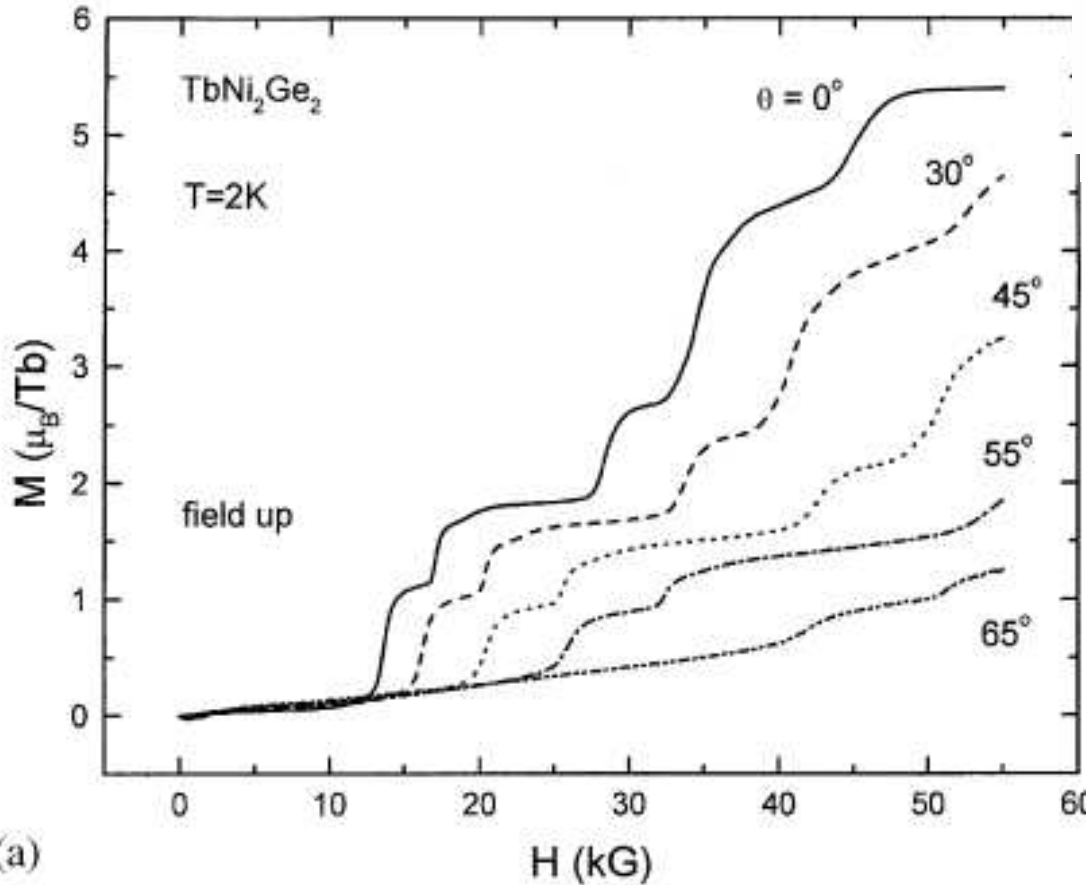




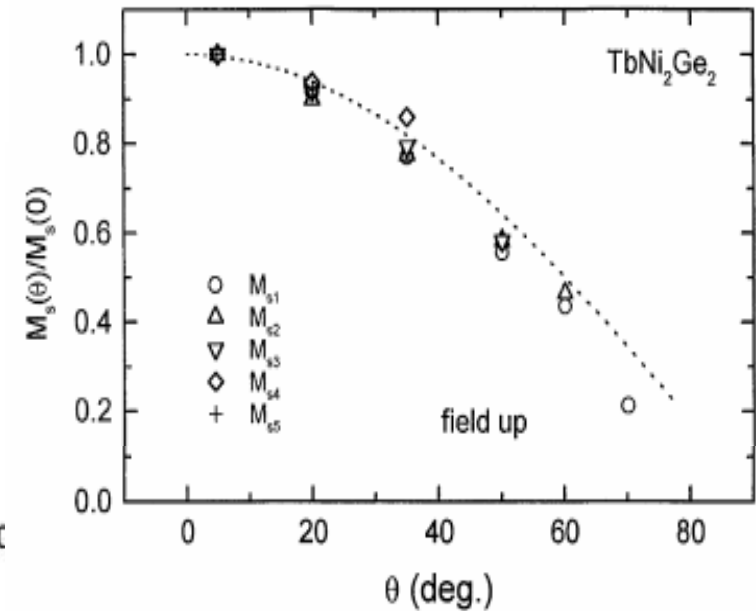
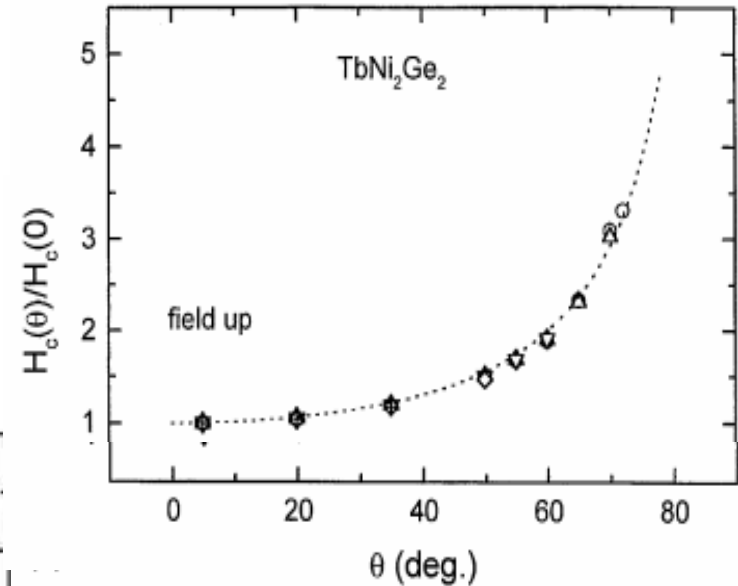
Angular dependent effects

$H_c \sim 1/\cos(\theta)$ (There is a critical field along the c-axis that must be exceeded.)

$M_{\text{sat}} \sim \cos(\theta)$ (The longitudinal moment is just the projection of easy axis moment along field direction.)



(a)

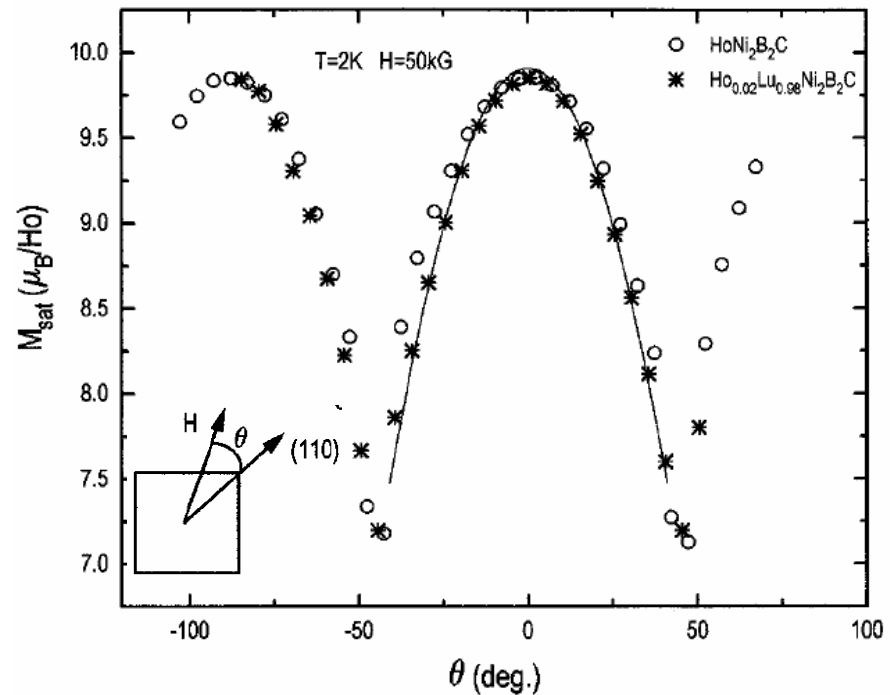
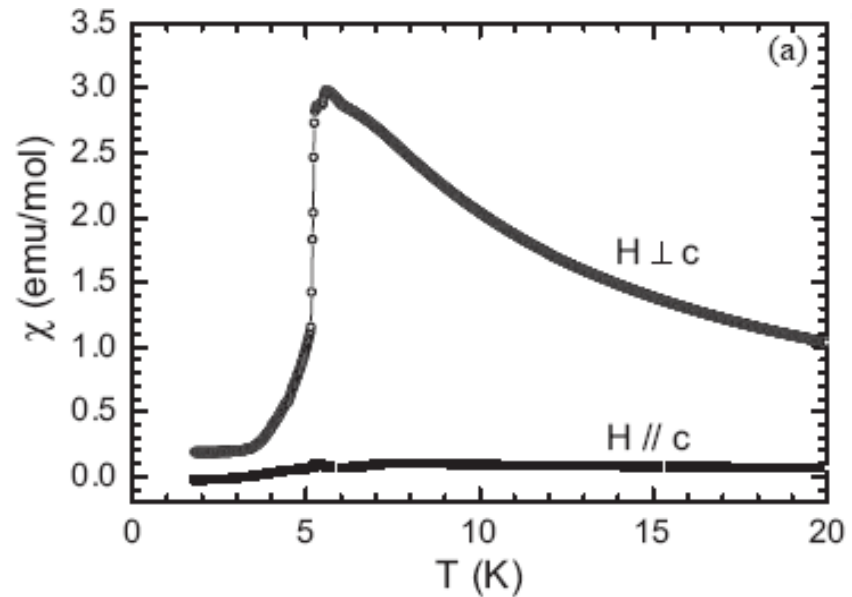




Angular dependent effects

$\text{HoNi}_2\text{B}_2\text{C}$ manifests a more interesting anisotropy. It is tetragonal and has Ho in a tetragonal point symmetry. At low temperatures the local moment is confined to the basal plane.

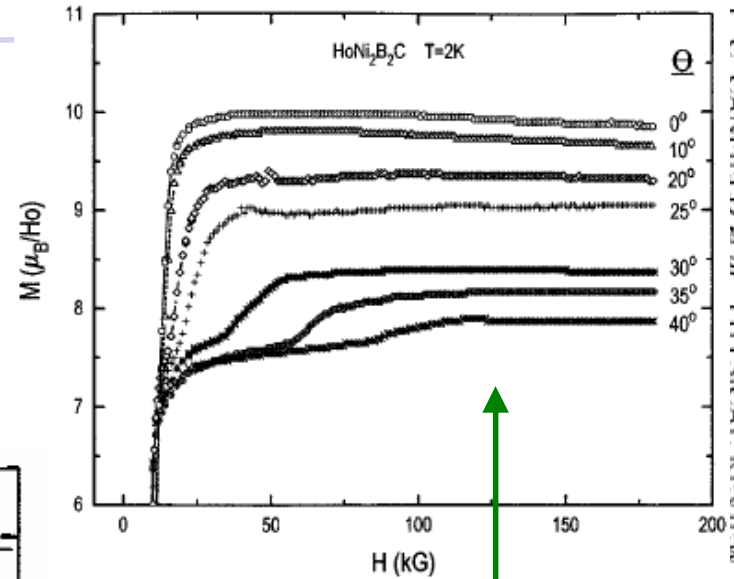
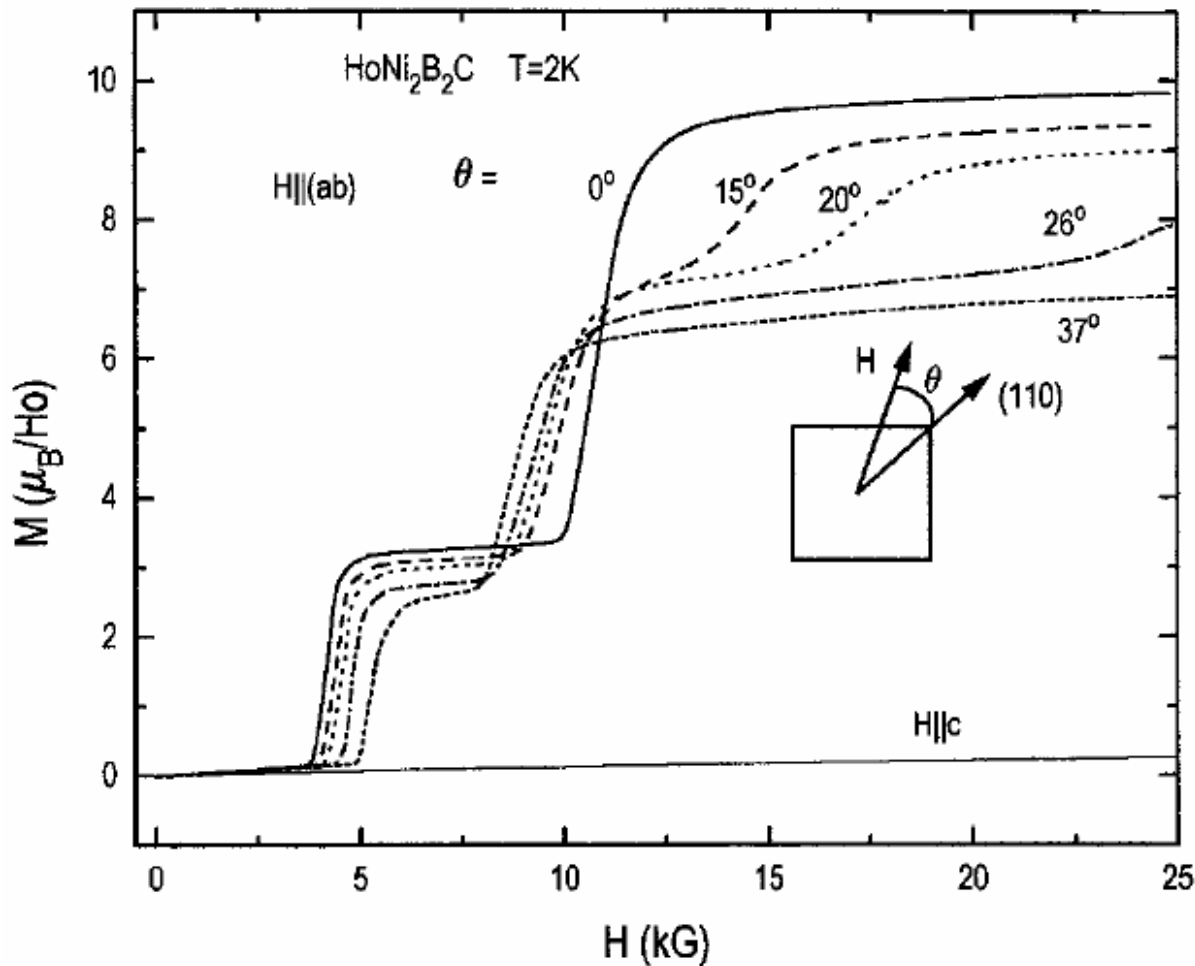
Until recently there was a prejudice that if the local moment was not Ising in nature, then it would be x-y, meaning that there would be no anisotropy in the easy plane....We found a very different situation: a 4-state clock system: the moments only point N, S, E, W; or up, down, right, left; or along the four (110) directions.





Angular dependent effects

The $T < T_N$ $M(H)$ data show clear, *in-plane* anisotropies with three metamagnetic transitions that vary with θ .

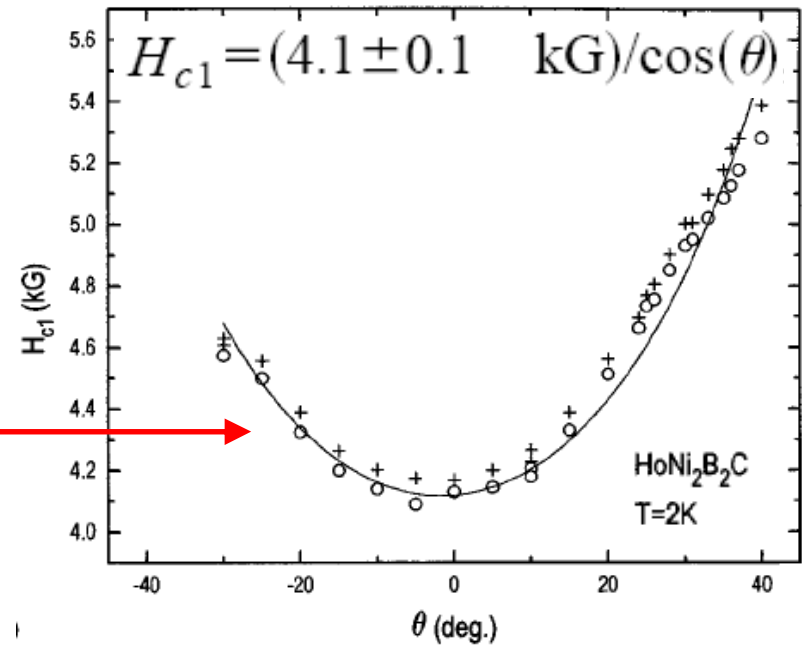
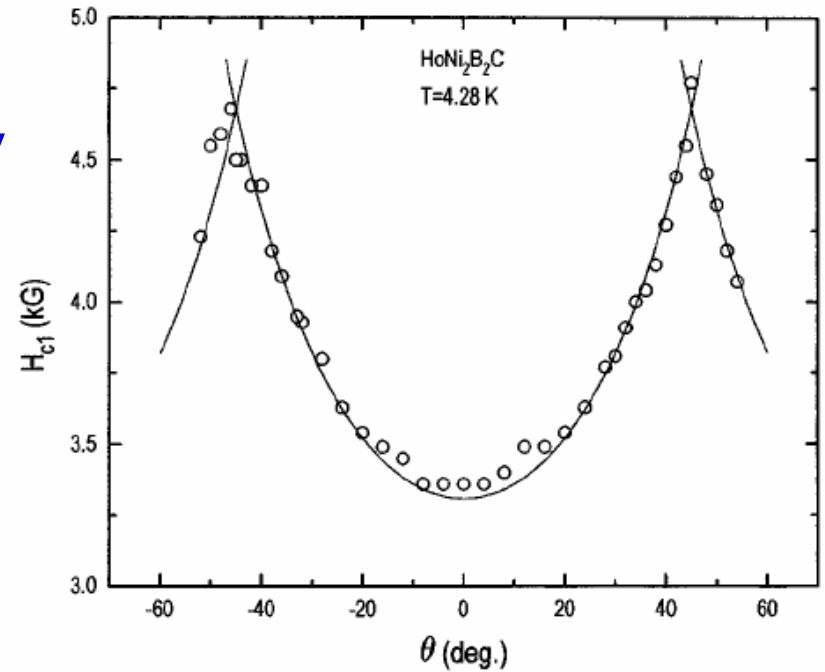
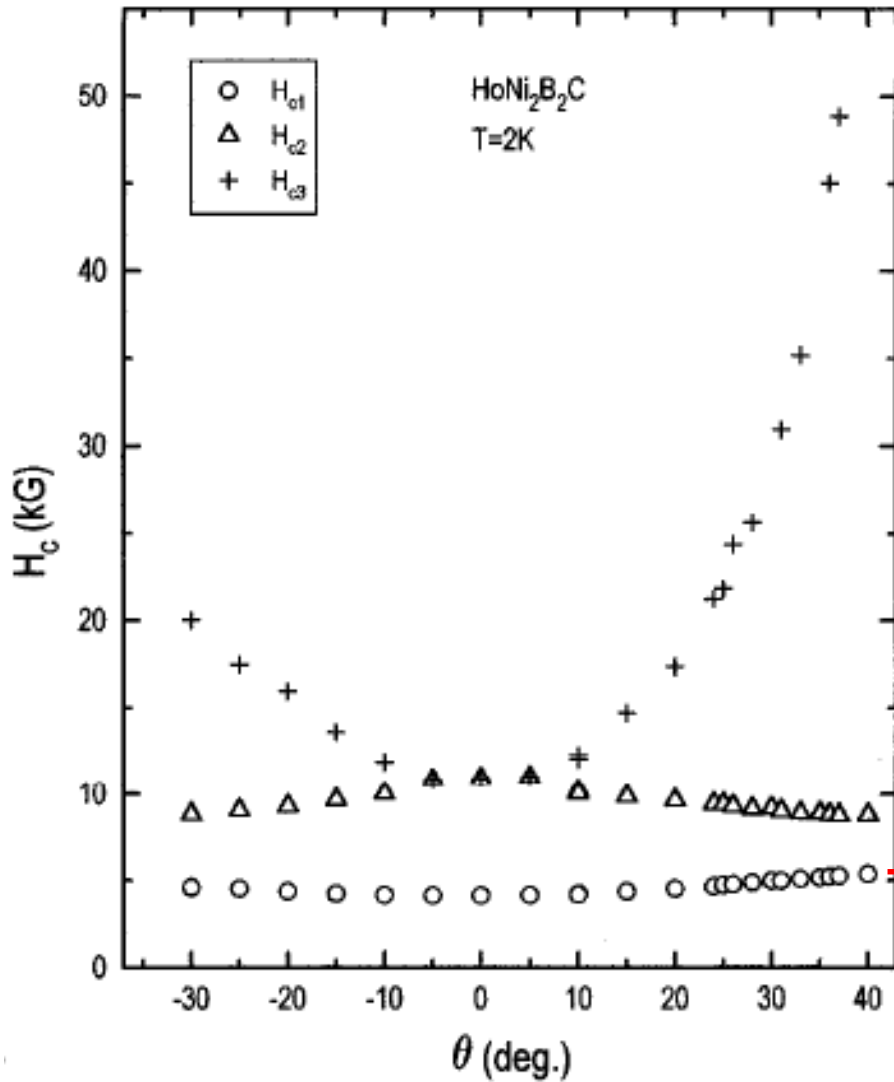


The highest field transition appears to diverge as H approaches the (111) direction

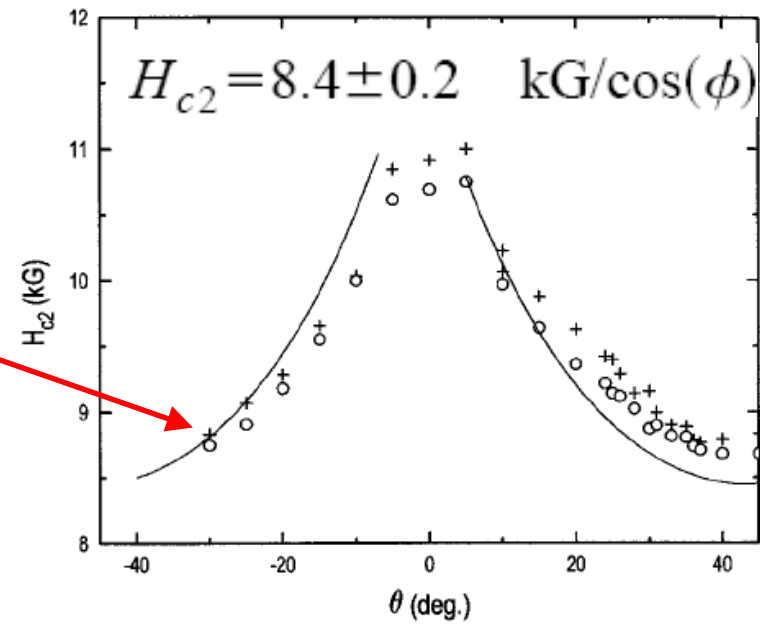
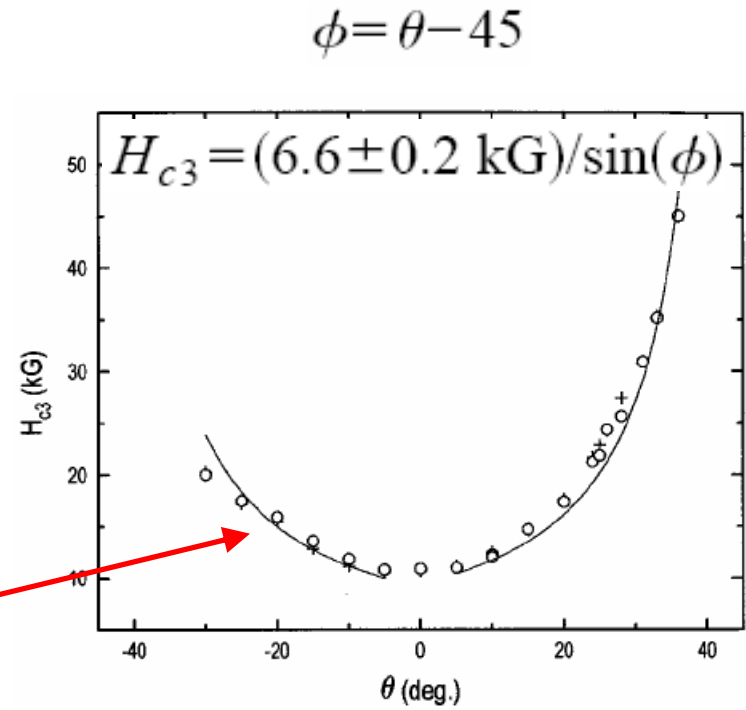
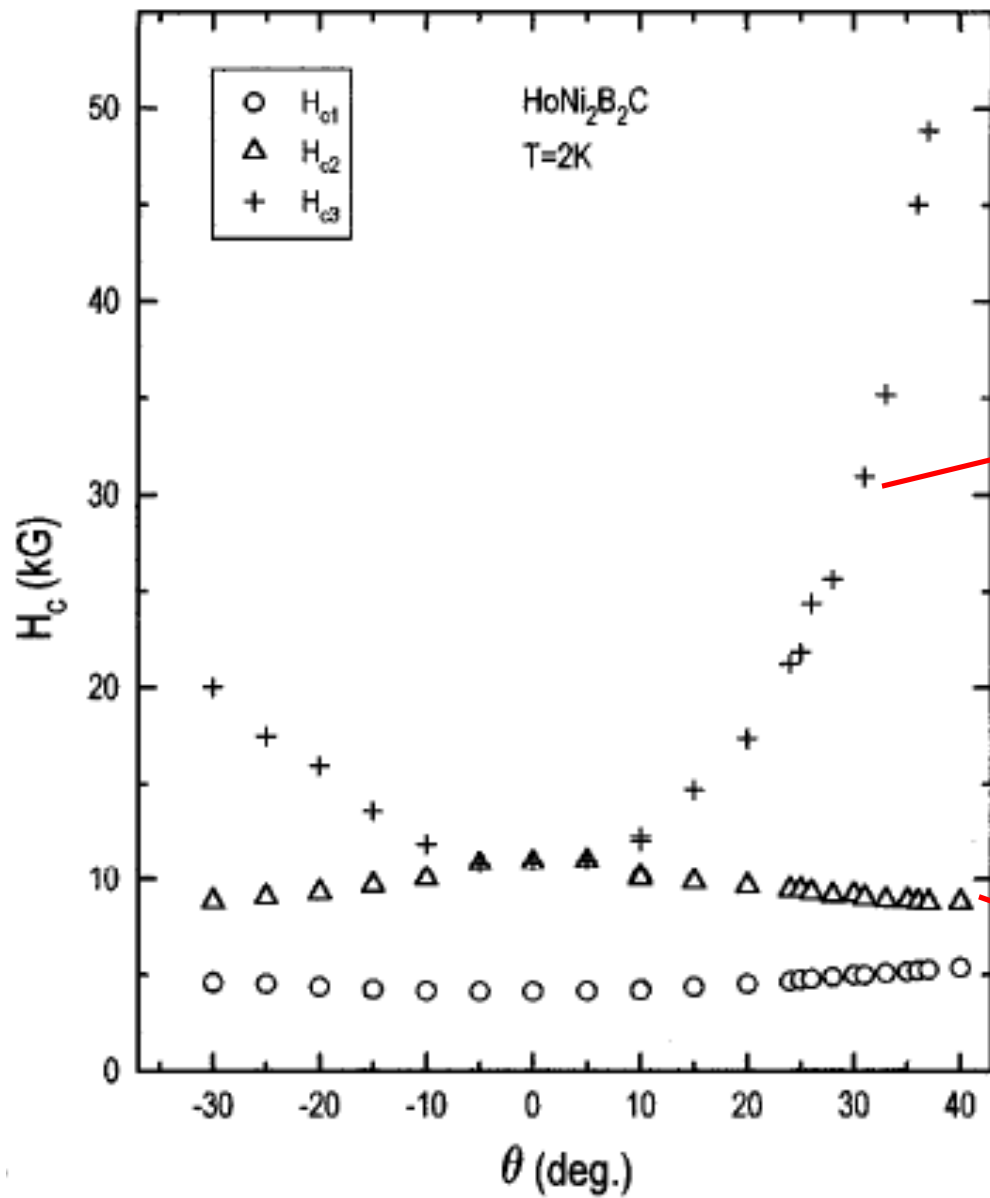


Angular dependent effects

All three critical fields show compellingly simple angular dependencies.



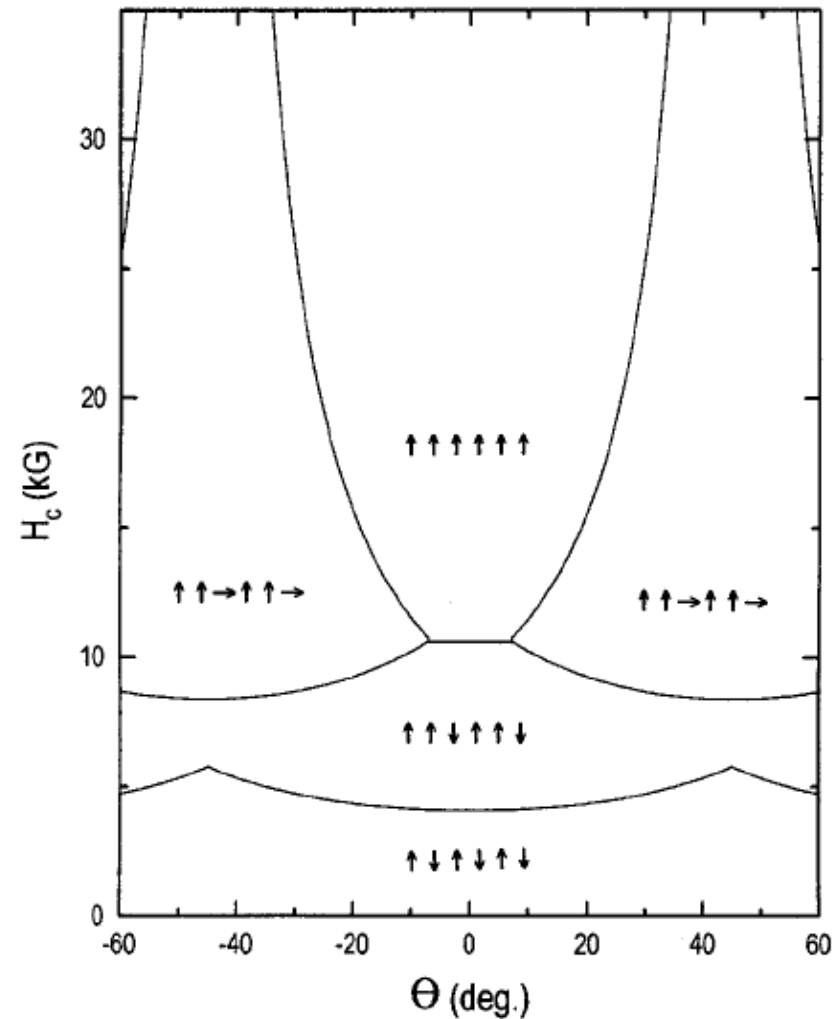
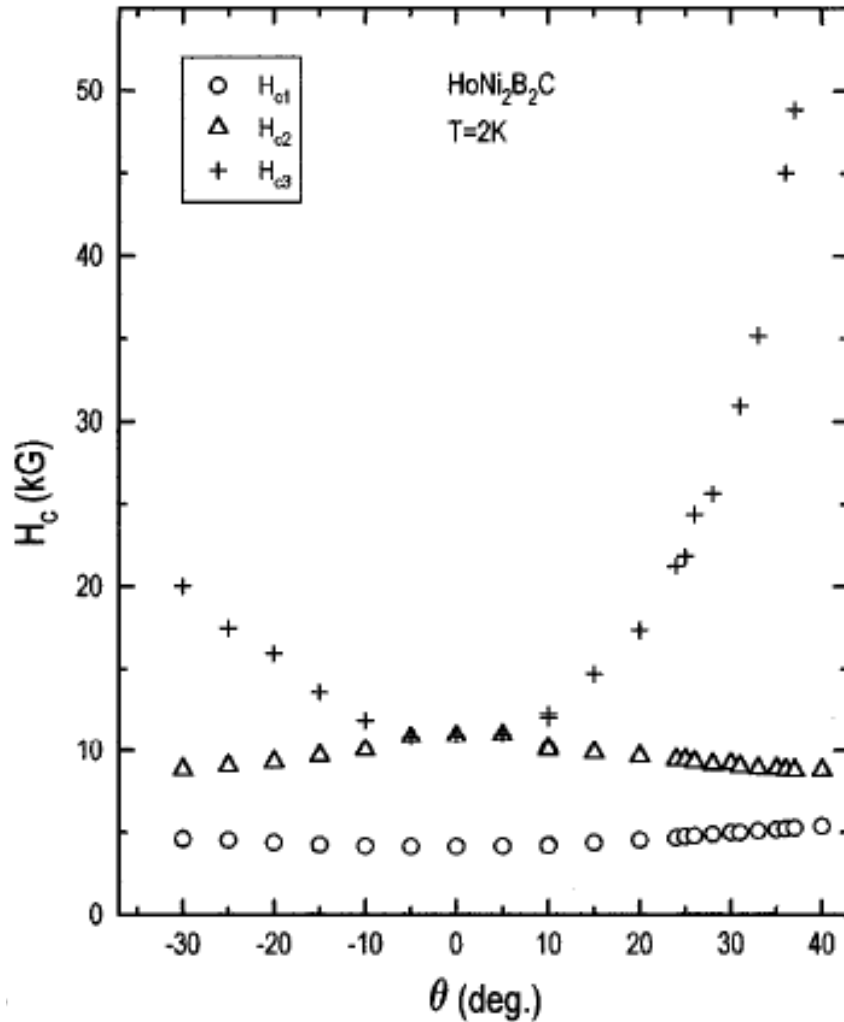
Angular dependent effects





Angular dependent effects: $H - \theta$ phase diagrams

These angular dependencies can be easily captured by assuming that each state consists of a net distribution of highly anisotropic moments along the four, in-plane easy axes.





Summary

This lecture has reviewed how to map, identify and start to describe regions of H-T (and in the end H- θ) phase space with three simple measurement techniques:

$$\rho(T, H, \theta),$$

$$C_p(T, H, \theta),$$

$$M(T, H, \theta).$$

These techniques combined with the ability to design, discovery, and grow novel compounds opens the way to the discovery and description of novel physics.



What else can we do? (part 1)

More advanced data with basically the same measurements:

Magneto-transport

$\rho(H)$ and Kohler's rule

Hall effect

Quantum oscillations

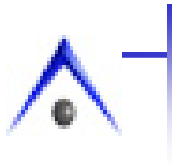
dHvA measurements in $M(H)$

SdH measurements in $\rho(H)$

Other measurements that are basic and useful:

Thermoelectric power

Thermal Conductivity



What else can we do? (part 2)

Extremes that help us learn more by changing energy ratios:

Low T: down to 1.5 K, down to 0.3 K, down to 0.03 K. Each gets harder and more expensive.

High d.c. magnetic field: 5 T, 10 T, 15 T, 20 T. Each step doubles cost (or more)

Pulsed magnetic fields: 30 T, 60 T, 90 T

Extremes help us learn more by controllably perturbing the sample:

Pressure: use of hydrostatic pressure to tune compounds is clean and useful. 10 – 30 kbar is not too hard, 30 – 100 kbar is difficult, and greater than 100 kbar is very difficult. Resistivity under pressure is the easiest measurement. Low pressure (~ 10 kbar) magnetic susceptibility, χ , is not too hard either.

Some of these measurements can be done in your own lab, some with friends, some at specialized facilities.



That's All Folks