$R_5(Si_xGe_{1-x})_4$

AN IDEAL SYSTEM TO BE STUDIED IN X-RAY AT HIGH MAGNETIC FIELD

P. A. Algarabel[1], C. Magén[1*], L. Morellón[1] and M. R. Ibarra[1]

[1]Instituto de Ciencia de Materiales de Aragón, ICMA
CSIC-Universidad de Zaragoza, Zaragoza 5009, Spain

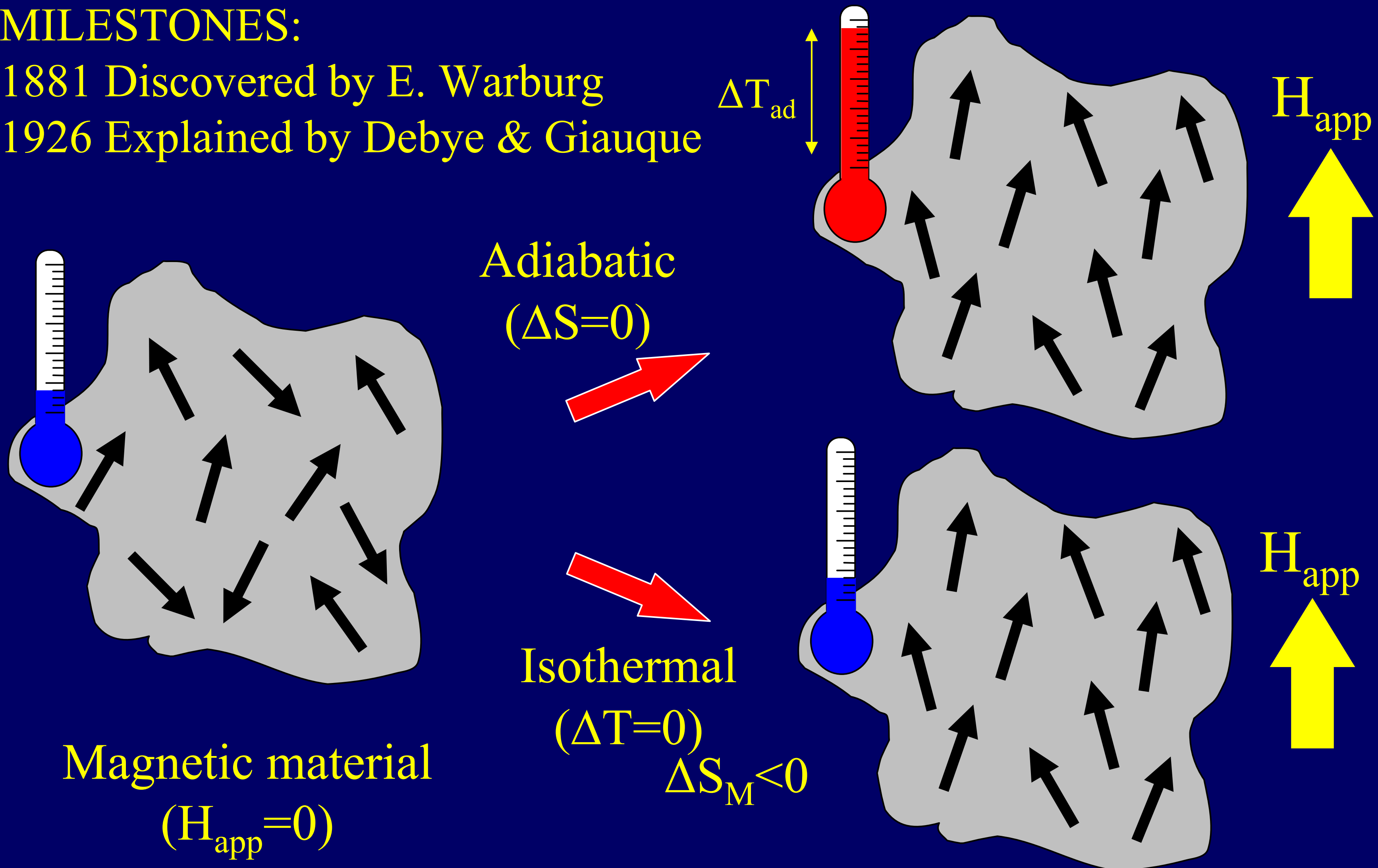
*CEMES-CNRS, Toulouse, France

Outline

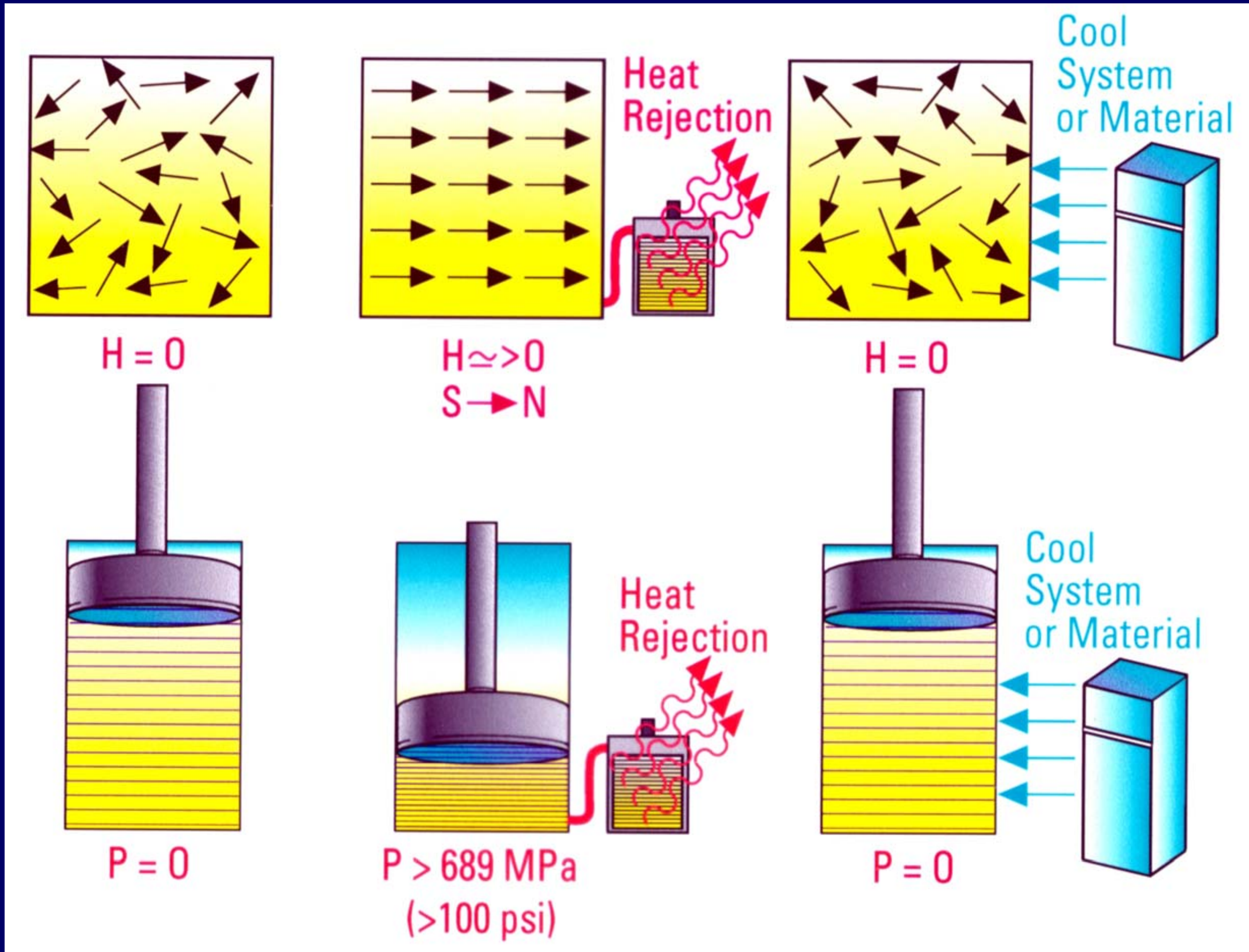
- ► Introduction to the $R_5(Si_xGe_{1-x})_4$ alloys:
  - ➢ Giant magnetocaloric effect (GMCE) & magnetic refrigeration.
  - ➢ Origin of GMCE – Field-induced magnetostructural transitions.
- ► Magnetostructural effects in $R_5(Si_xGe_{1-x})_4$
  - ➢ $Gd_5(Si_xGe_{1-x})_4$
  - ➢ $Tb_5(Si_xGe_{1-x})_4$
  - ➢ Er_5Si_4
- ► Conclusions
- ► Use of X-ray & magnetic field in 5:4 alloys?

The Magnetocaloric Effect (MCE)

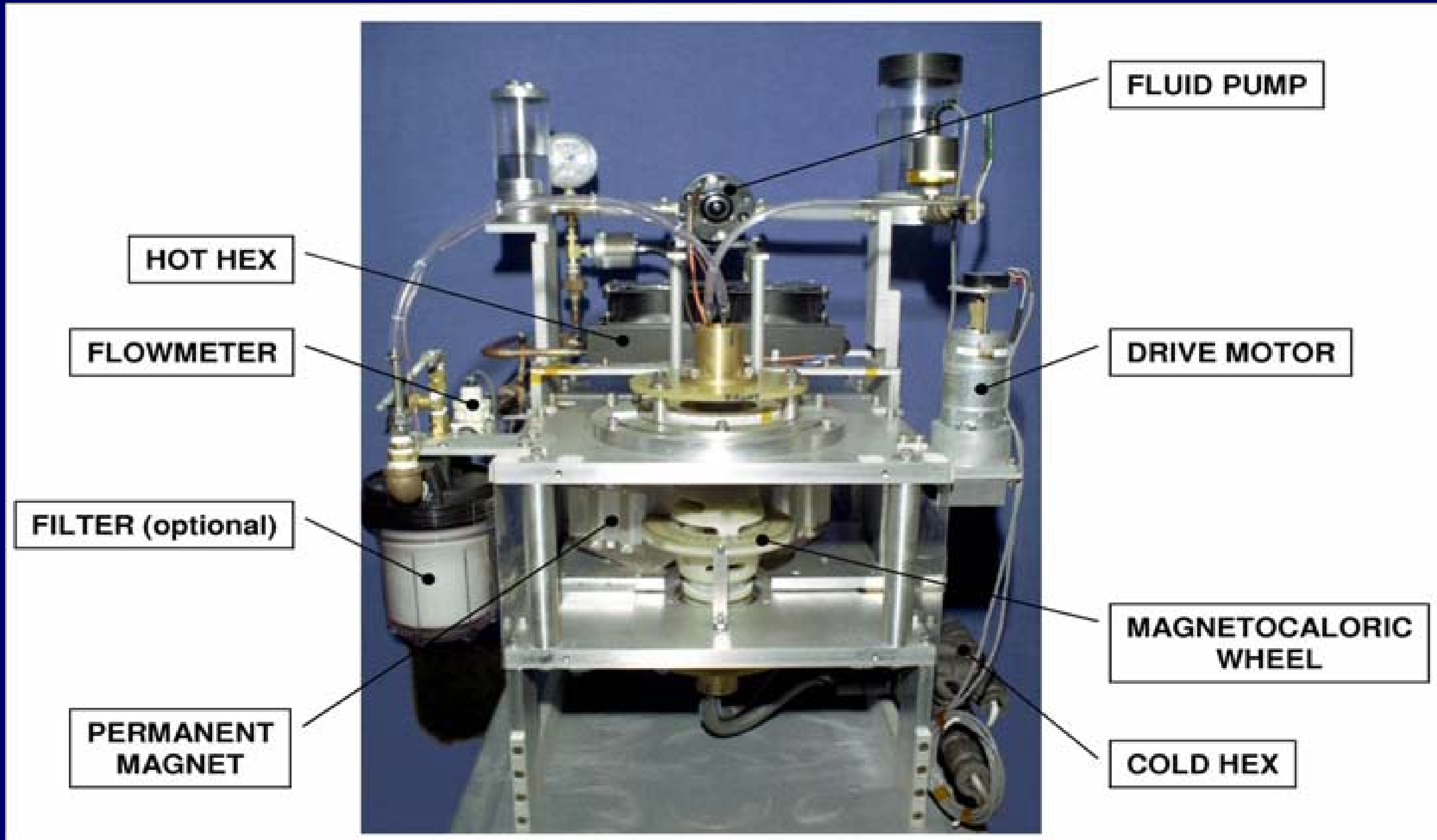
MILESTONES:
1881 Discovered by E. Warburg
1926 Explained by Debye & Giauque



MCE & Magnetic Refrigeration



Magnetic Refrigeration Technology



- Laboratory Prototype Refrigerator (2001).
- Permanent Magnet Rotary Device - 1 Hz (in 2004 update, 4 Hz).

(Astronautics Corporation of America, Milwaukee, Wisconsing, US)

$Gd_5(Si_xGe_{1-x})_4$ – Giant MCE Compounds

VOLUME 78, NUMBER 23 PHYSICAL REVIEW LETTERS 9 JUNE 1997

Giant Magnetocaloric Effect in $Gd_5(Si_2Ge_2)$

V. K. Pecharsky and K. A. Gschneidner, Jr.
Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-3020
(Received 22 November 1996)

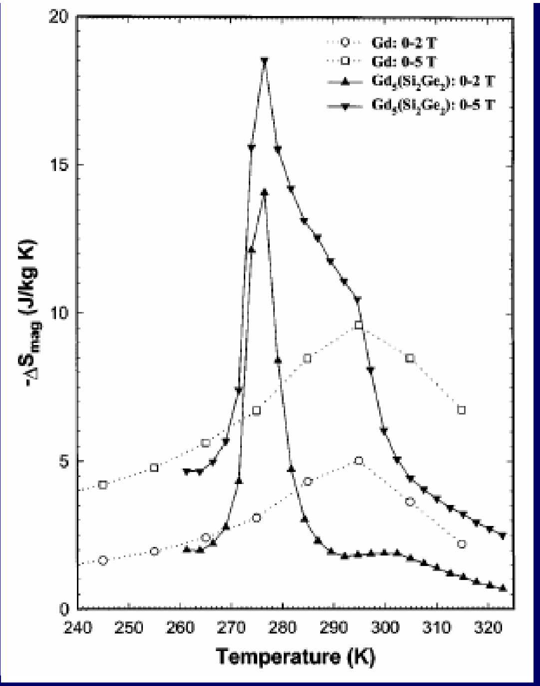
An extremely large magnetic entropy change has been discovered in $Gd_5(Si_2Ge_2)$ when subjected to a change in the magnetic field. It exceeds the *reversible* (with respect to an alternating magnetic field) magnetocaloric effect in any known magnetic material by at least a factor of 2, and it is due to a first order [ferromagnetic (I) ↔ ferromagnetic (II)] phase transition at 276 K and its unique magnetic field dependence. [S0031-9007(97)03321-8]

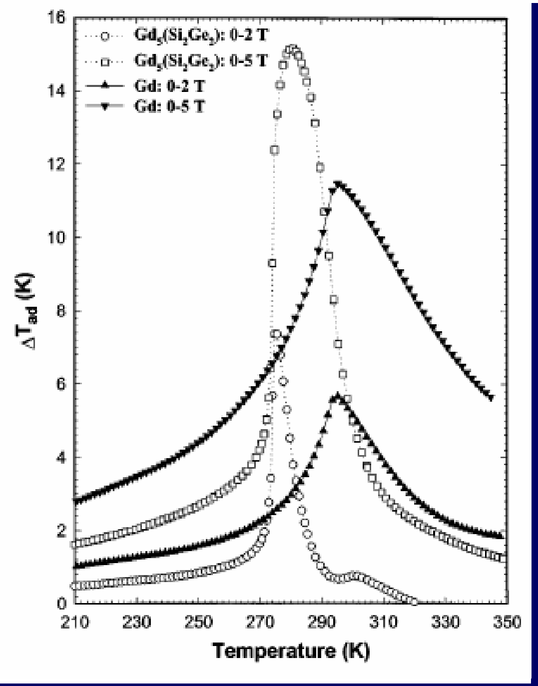
RECORD VALUES:

$-\Delta S_M = 36$ J/kg-K

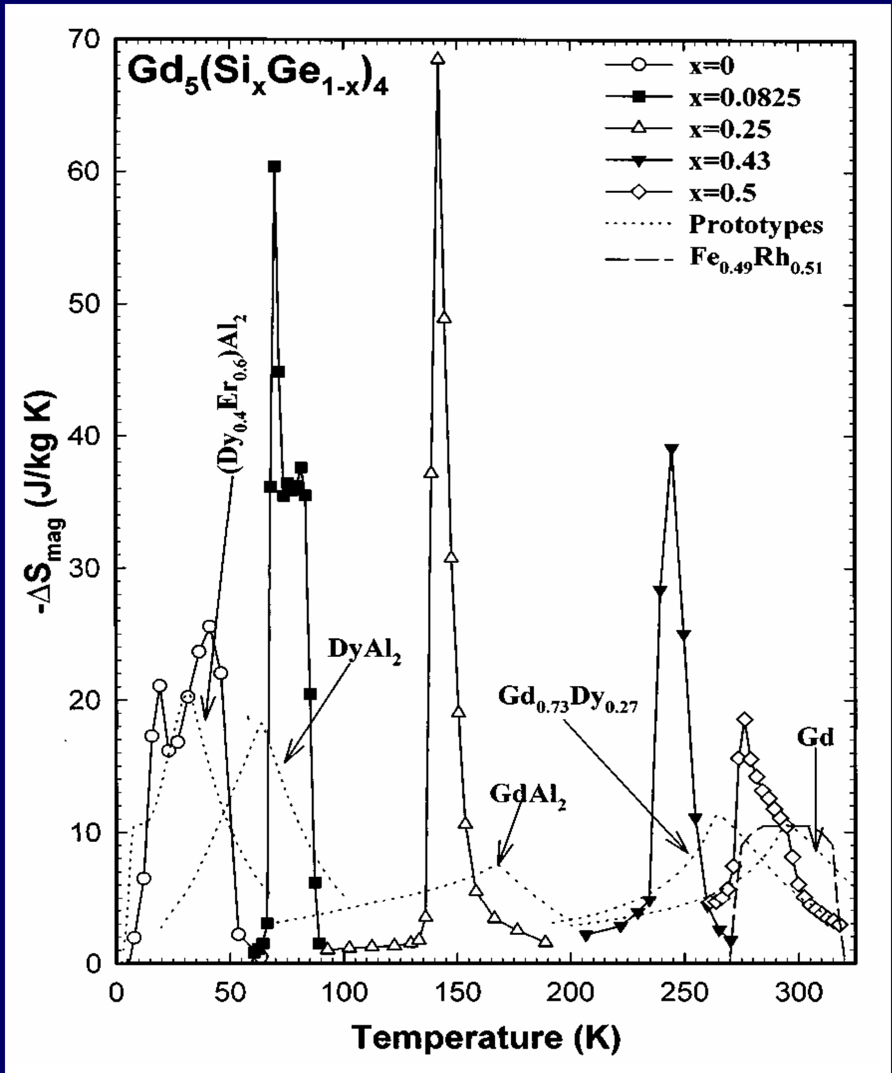
$\Delta T_{ad} = 17$ K

V. K. Pecharsky et al.
J. Appl. Phys. **93**, 4722 (2003)





$Gd_5(Si_xGe_{1-x})_4$ – Tunable GMCE



$Gd_5(Si_xGe_{1-x})_4$ $x \leq 0.5$

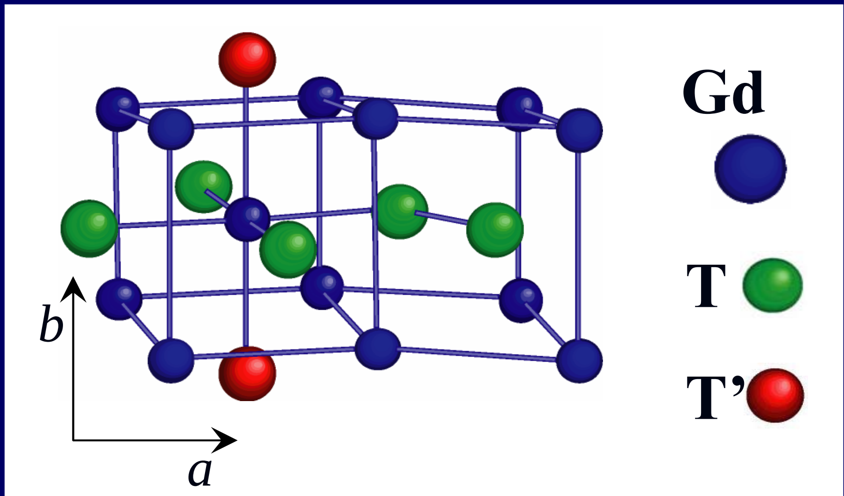
x	$-\Delta S_M$ (J/Kg-K)
0	20-25
0.0825	60
0.25	68
0.43	39
0.5	18

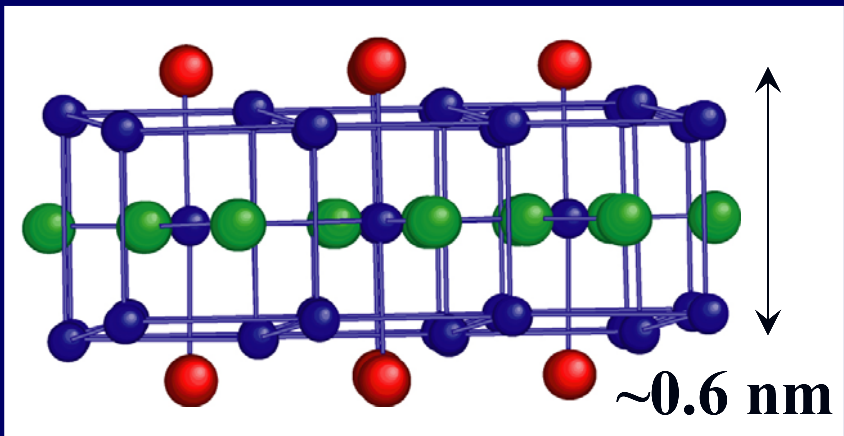
- Temperature tuning of GMCE by changing the Si/Ge ratio.

V. K. Pecharsky et al.
Appl. Phys. Lett. **70,** 24 (1997)

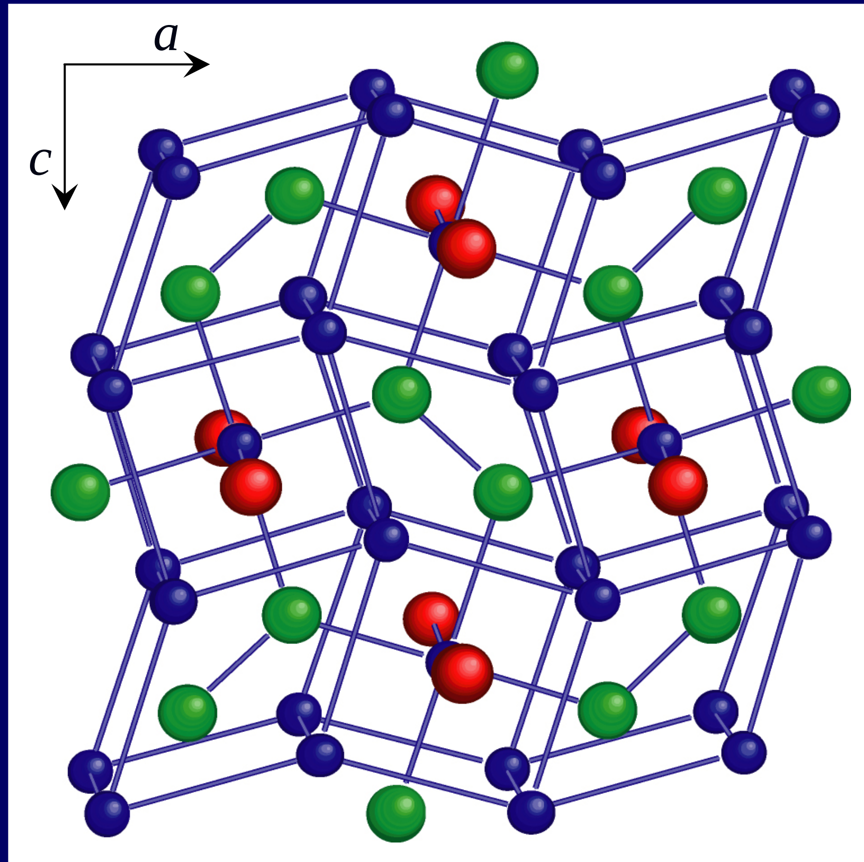
$Gd_5(Si_xGe_{1-x})_4$ – a Nanolayered Structure

Building blocks





2D layer - "slab"



$Gd_5(Si_xGe_{1-x})_4$ – 3D Structure & Bonding

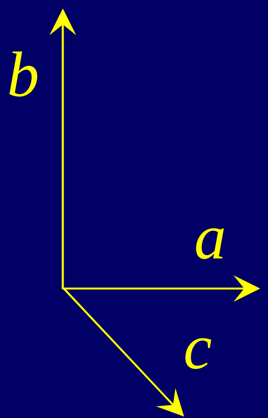
Orthorhombic	Monoclinic	Orthorhombic
Pnma [*O*(II)]	*P*112$_1$/a [*M*]	*Pnma* [*O*(I)]

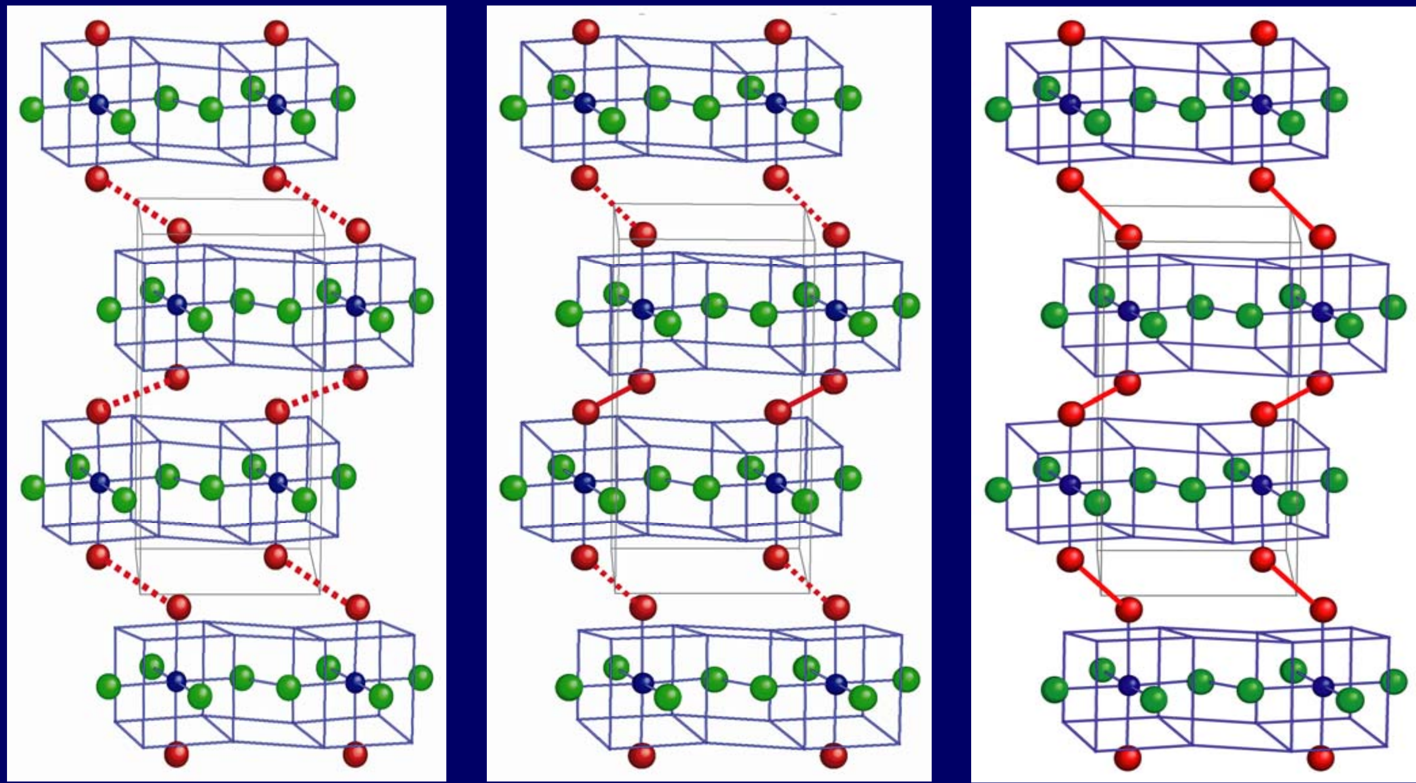
$a \approx 7.5$ Å

$b \approx 14.8$ Å

$c \approx 7.8$ Å

$V \approx 870$ Å^3



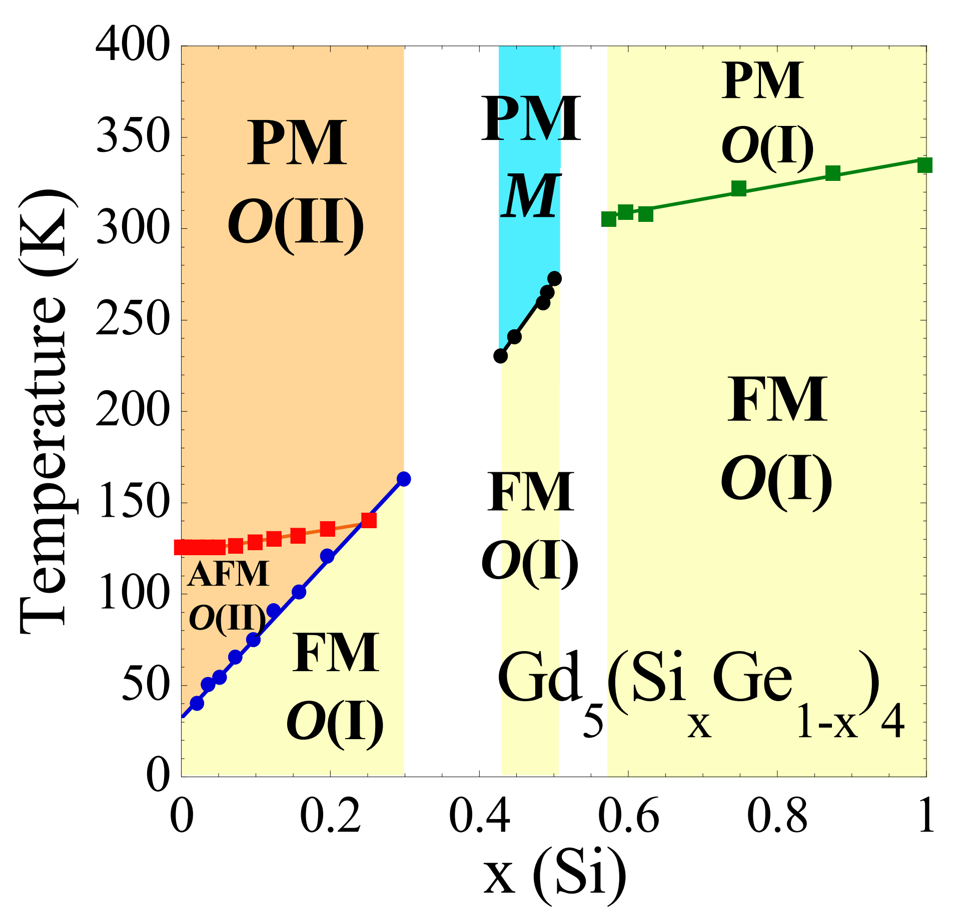


T′$_2$ (interlayer bond) ≈ 2.6 Å

T′-T′ (unbonded pair) ≈ 3.5 Å

Δ ≈ 33%

$Gd_5(Si_xGe_{1-x})_4$ – Structure & Magnetism

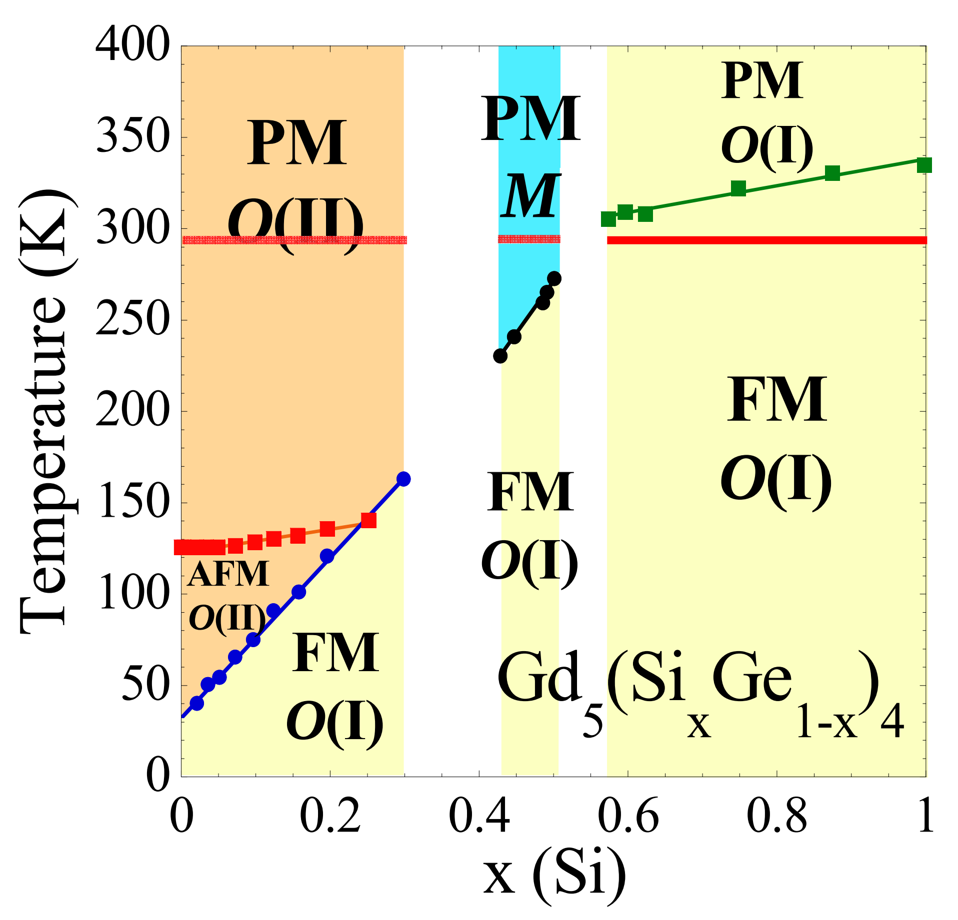


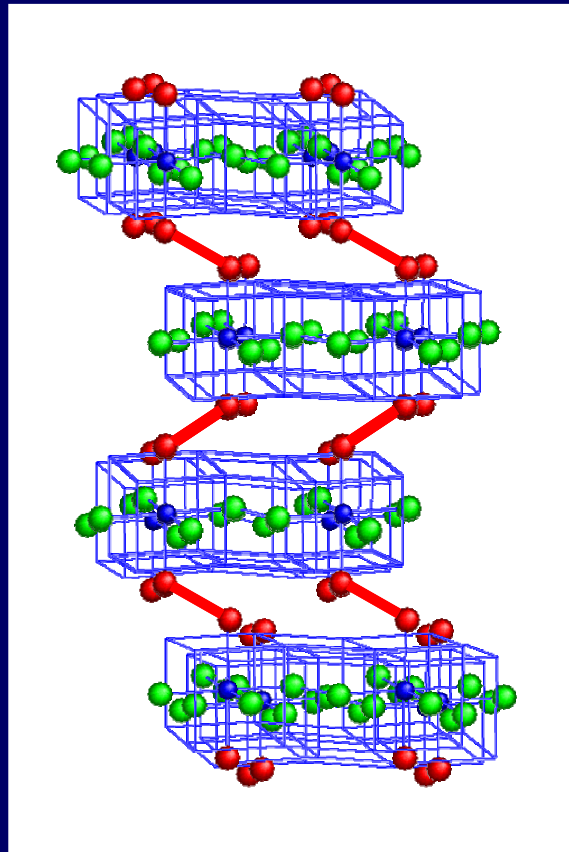
V. K. Pecharsky et al., Appl. Phys. Lett. **70**, 3299 (1997)
L. Morellon et al., Phys. Rev. B **62**, 1022 (2000)
A. O. Pecharsky et al., J. All. & Comp. **338**, 126 (2002)
W. Choe et al. Phys. Rev. Lett. **84**, 4617 (2000)

Three solid-solution regions:

- Sm_5Ge_4-type, *O*(II)
  Ge-rich ($0 < x \leq 0.3$)
- $Gd_5Si_2Ge_2$-type, *M*
  Intermediate ($0.4 < x \leq 0.5$)
- Gd_5Si_4-type, *O*(I)
  Si-rich ($0.575 \leq x \leq 1$)
  &
  Low T Ground State ($0<x\leq1$)

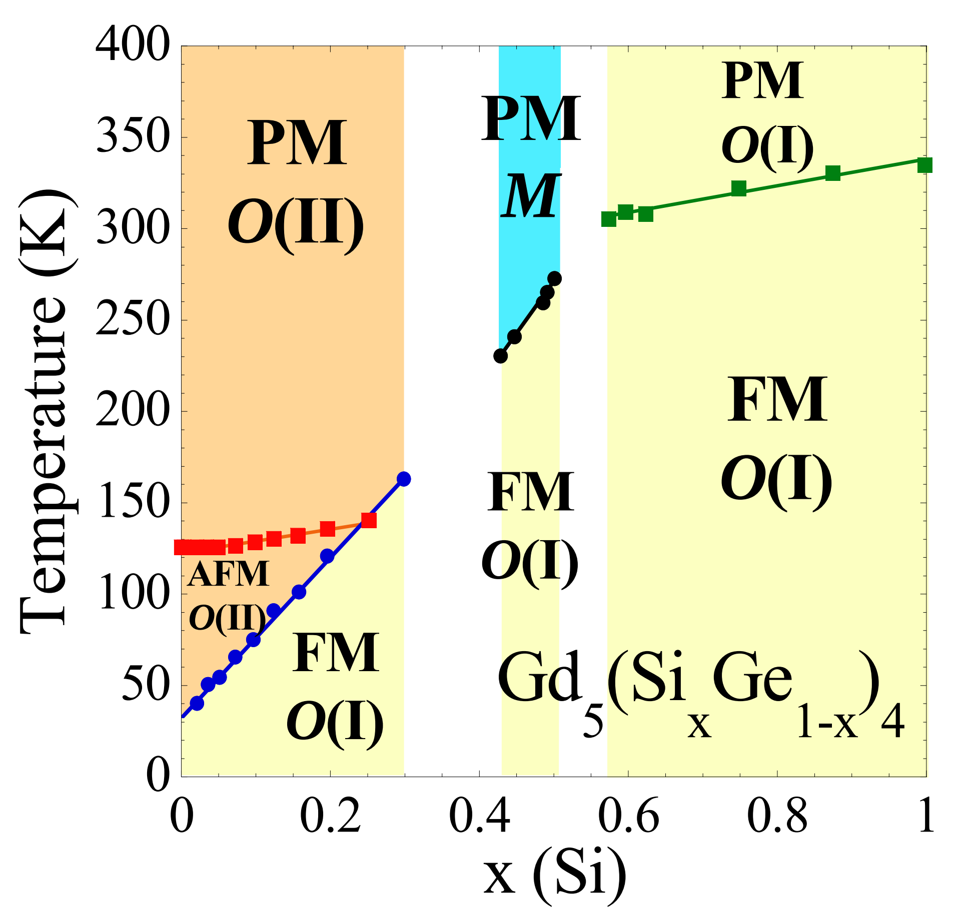
$Gd_5(Si_xGe_{1-x})_4$ – Structure & Magnetism





V. K. Pecharsky et al., Appl. Phys. Lett. **70**, 3299 (1997)
L. Morellon et al., Phys. Rev. B **62**, 1022 (2000)
A. O. Pecharsky et al., J. All. & Comp. **338**, 126 (2002)
W. Choe et al. Phys. Rev. Lett. **84**, 4617 (2000)

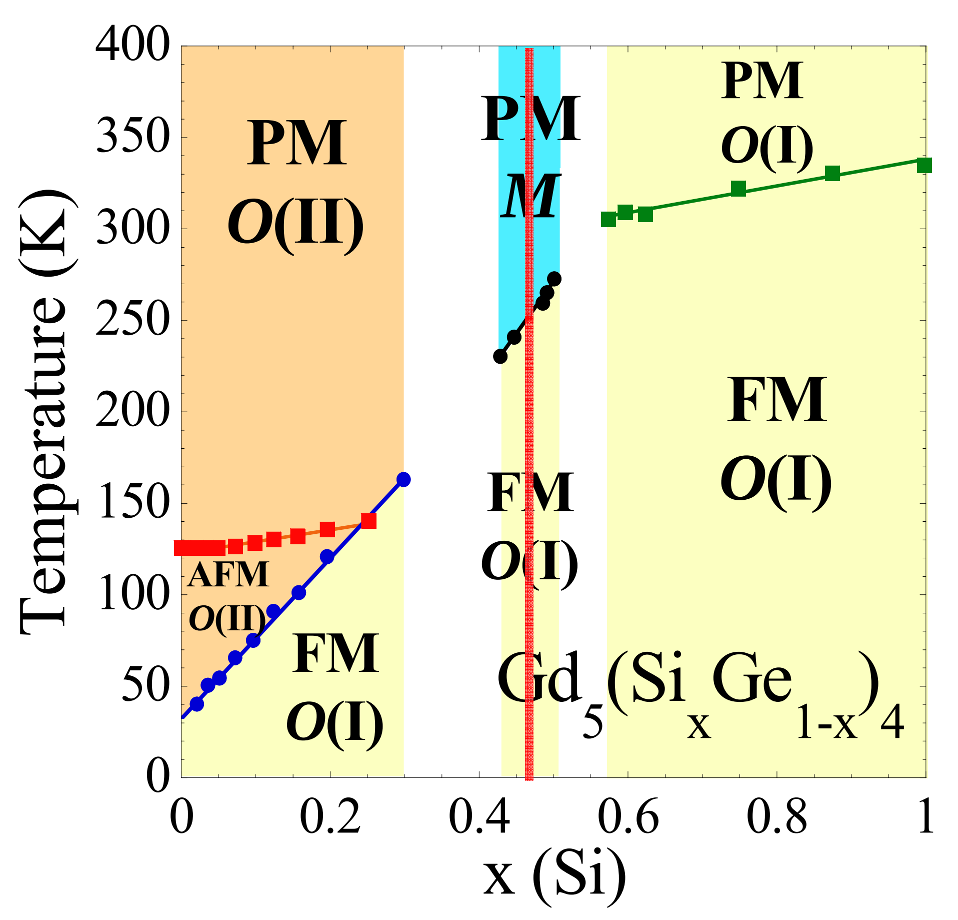
$Gd_5(Si_xGe_{1-x})_4$ – Structure & Magnetism

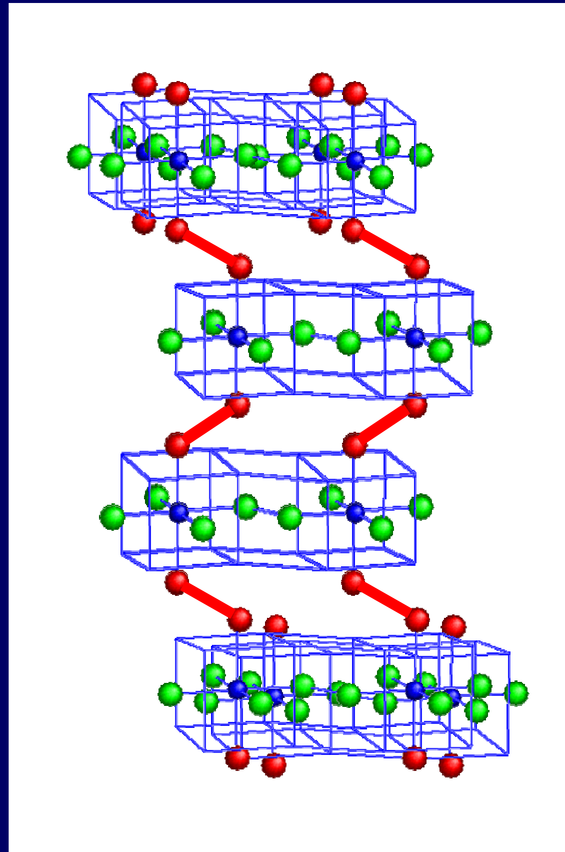


- ► The number of T'_2 bonds governs the competition between magnetic interactions:
- ● intralayer (4f-indirect RKKY exchange)
- ● interlayer (FM) (Gd-T'_2-Gd superexchange-like)
- ➢ Formation of T'_2 induces 3D FM
- ➢ T_C(Si-rich) > T_C(Gd) = 294 K

V. K. Pecharsky et al., Appl. Phys. Lett. **70**, 3299 (1997)
L. Morellon et al., Phys. Rev. B **62**, 1022 (2000)
A. O. Pecharsky et al., J. All. & Comp. **338**, 126 (2002)
W. Choe et al. Phys. Rev. Lett. **84**, 4617 (2000)

$Gd_5(Si_xGe_{1-x})_4$ – Structure & Magnetism



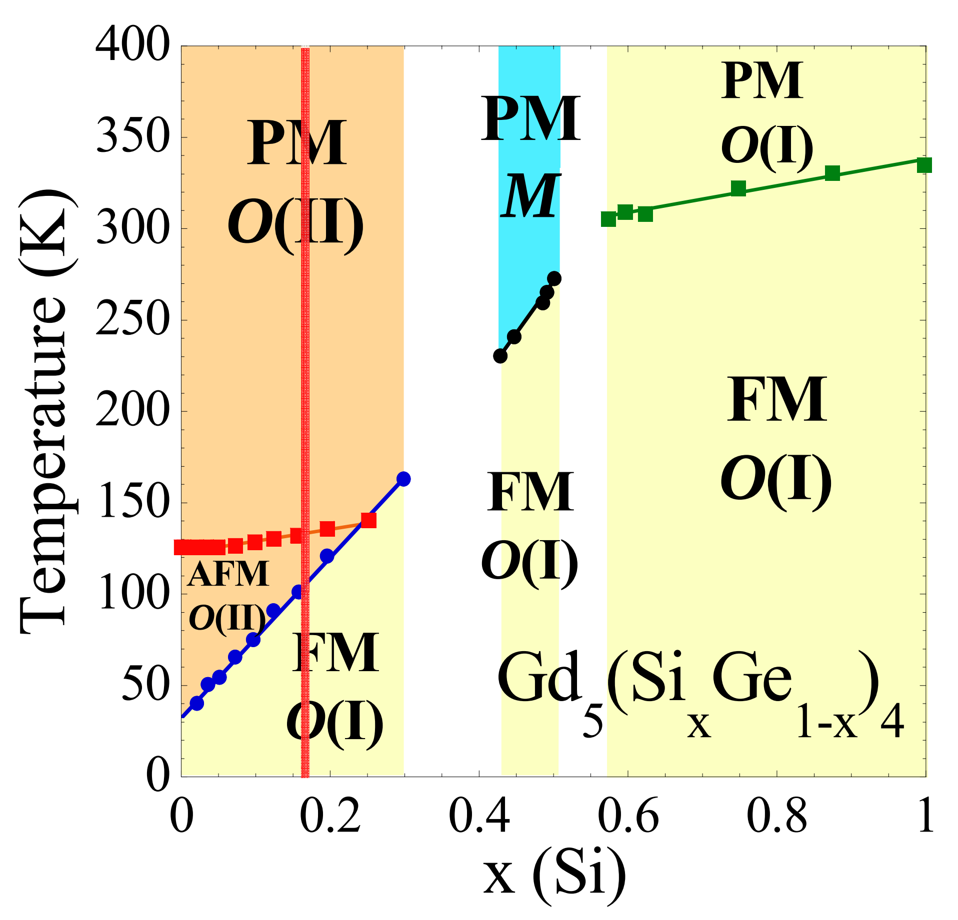


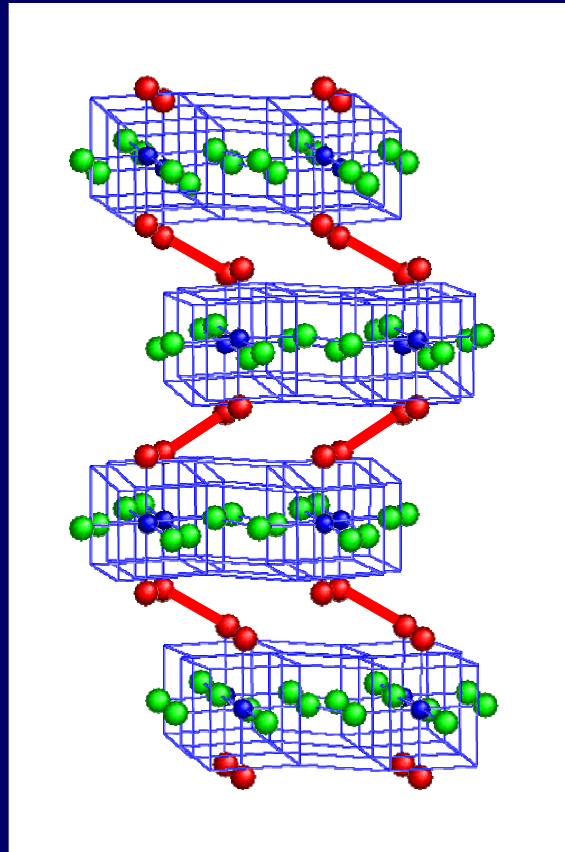
- Intermed. $0.4 < x \leq 0.503$
  M-PM → *O*(I)-FM
  i.e. x = 0.5 → $\Delta V/V \approx -0.4$ %

$\Delta a/a \approx -0.9$ %
$\Delta b/b \approx -0.1$ %
$\Delta c/c \approx +0.2$ %

- REVERSIBLE
- MAGNETOSTRUCTURAL
- 1st - ORDER TRANSITION

$Gd_5(Si_xGe_{1-x})_4$ – Structure & Magnetism





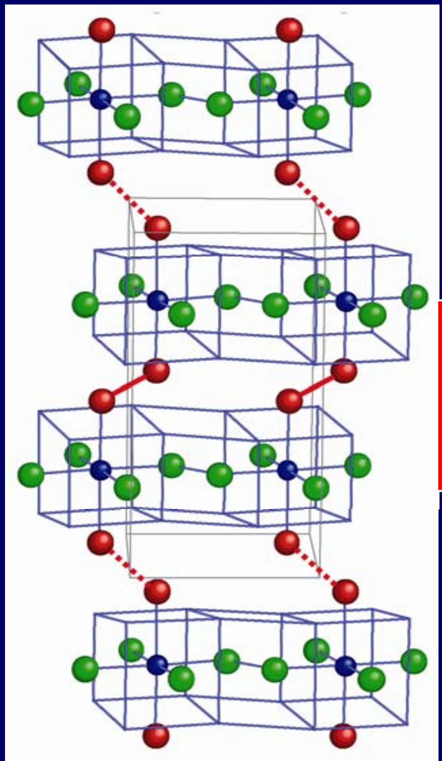
- Ge-rich $0 < x \le 0.3$
  O(II)-PM → AFM→*O*(I)-FM
  i.e. x = 0.1 → $\Delta V/V \approx -1$ %

$\Delta a/a \approx -1.6$ %
$\Delta b/b \approx -0.1$ %
$\Delta c/c \approx +0.5$ %

- ➢ REVERSIBLE
- ➢ MAGNETOSTRUCTURAL
- ➢ 1^{st} - ORDER TRANSITION

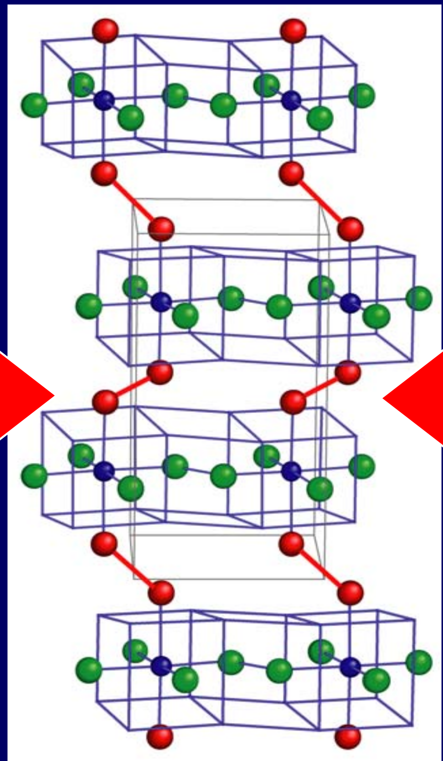
$Gd_5(Si_xGe_{1-x})_4$ – Magnetic Field Effects

M – PM



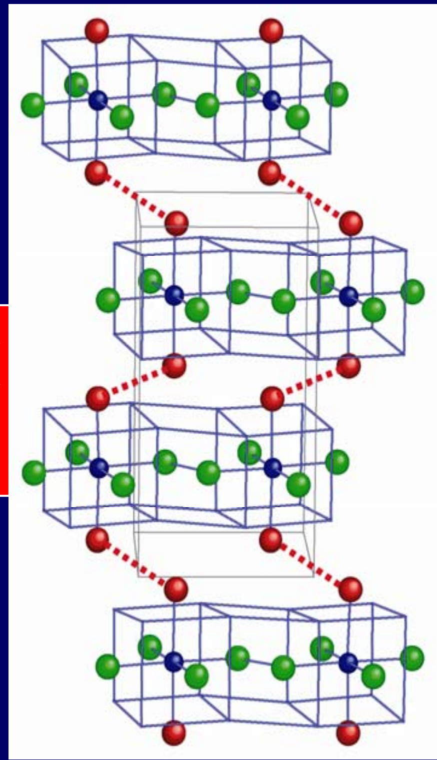
SWITCH FIELD →

O(I) – FM



← SWITCH FIELD

O(II) { PM, AFM }



MAGNETIC-FIELD-INDUCED TRANSITION at $T > T_C$ (T_N)

- REVERSIBLE
- MAGNETOSTRUCTURAL
- 1st - ORDER TRANSITION

$Gd_5(Si_xGe_{1-x})_4$ – Magnetic Field Effects

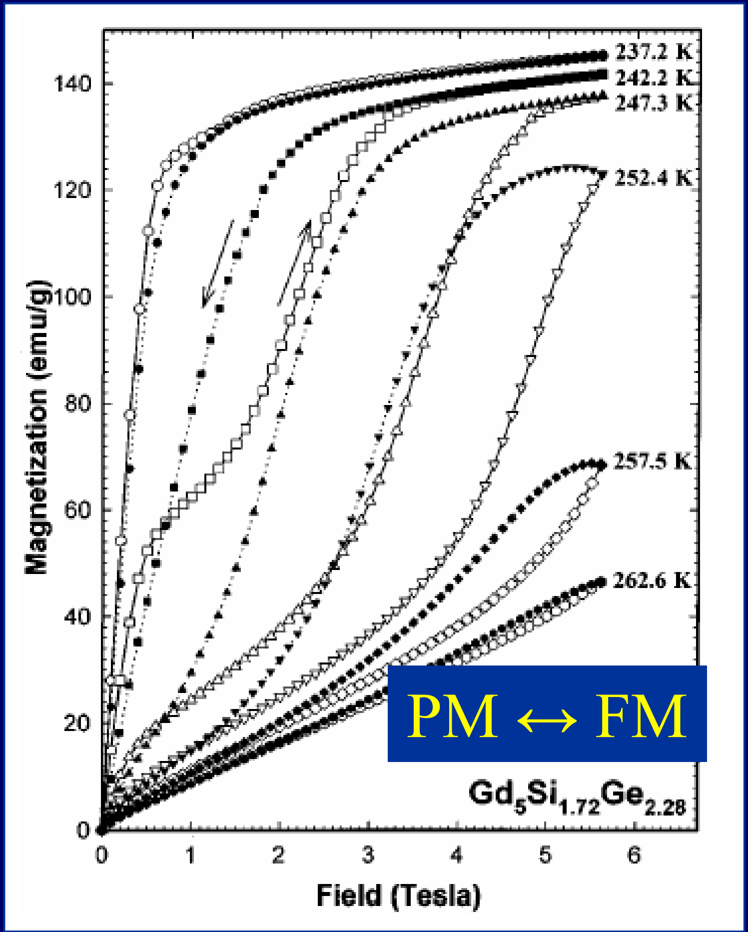
► Magnetostructural transition causes dramatic changes in:

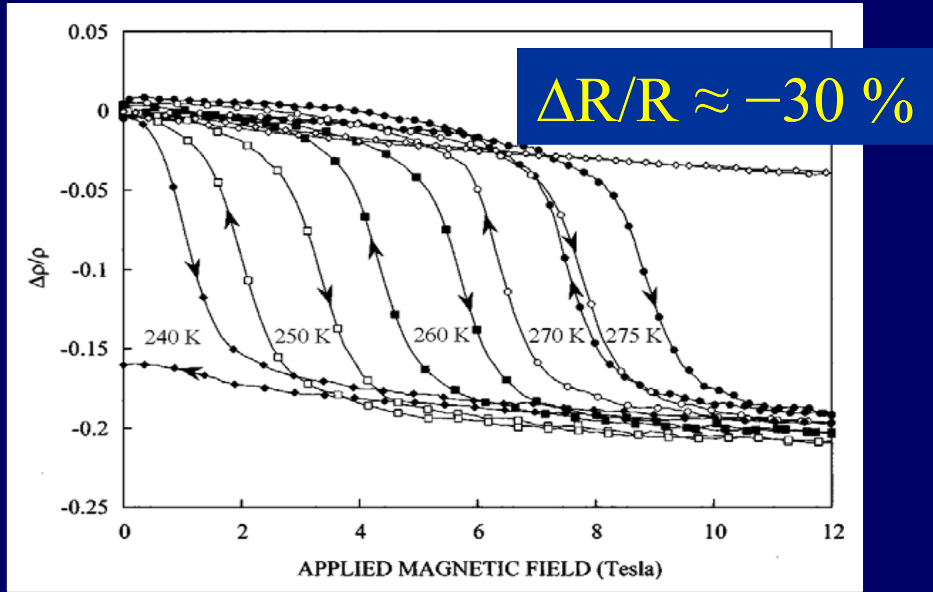
- Magnetism.
- Crystal structure (and chemical bonding!).
- Electronic Structure.

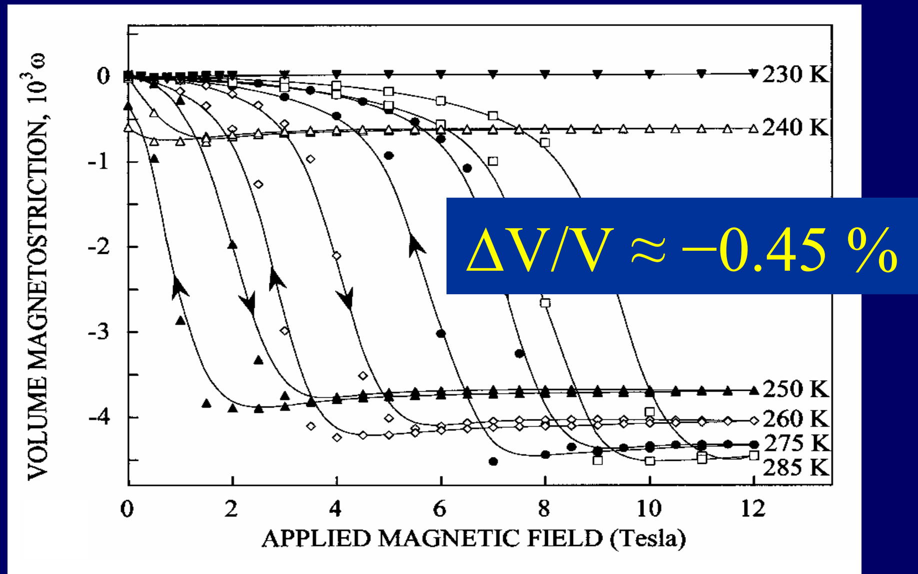
…and it is the origin of GMCE.

$$\Delta S_T = (\Delta S_{mag})_T + (\Delta S_{str})_T = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T} \right)_H + (\Delta S_{str})_T$$

$Gd_5(Si_xGe_{1-x})_4$ – Magnetic-field effects







V. K. Pecharsky et al, Appl. Phys. Lett. **70**, 3299 (1997)

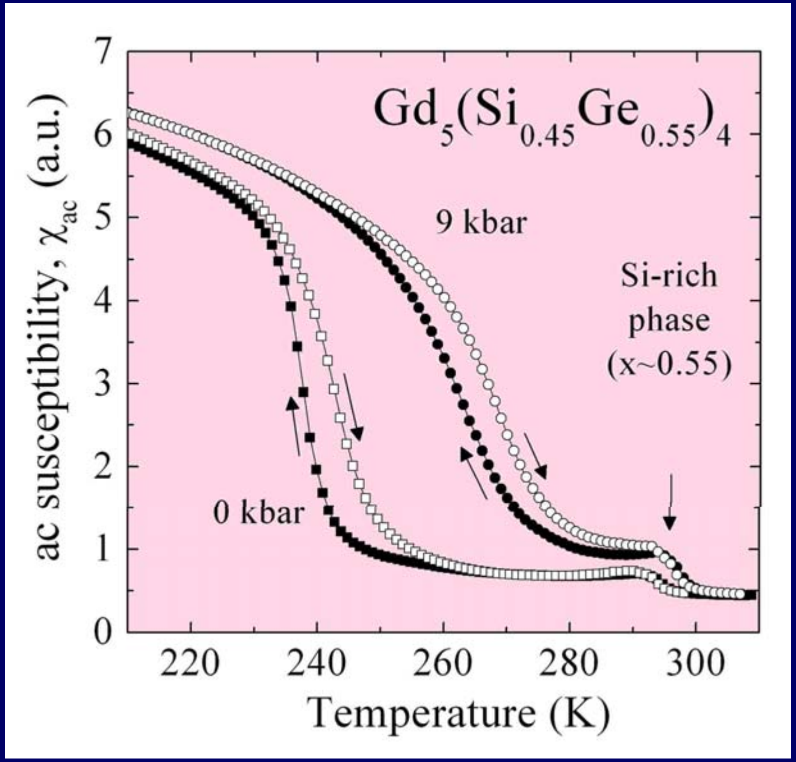
L. Morellon et al, Appl. Phys. Lett. **73**, 3463 (1998)

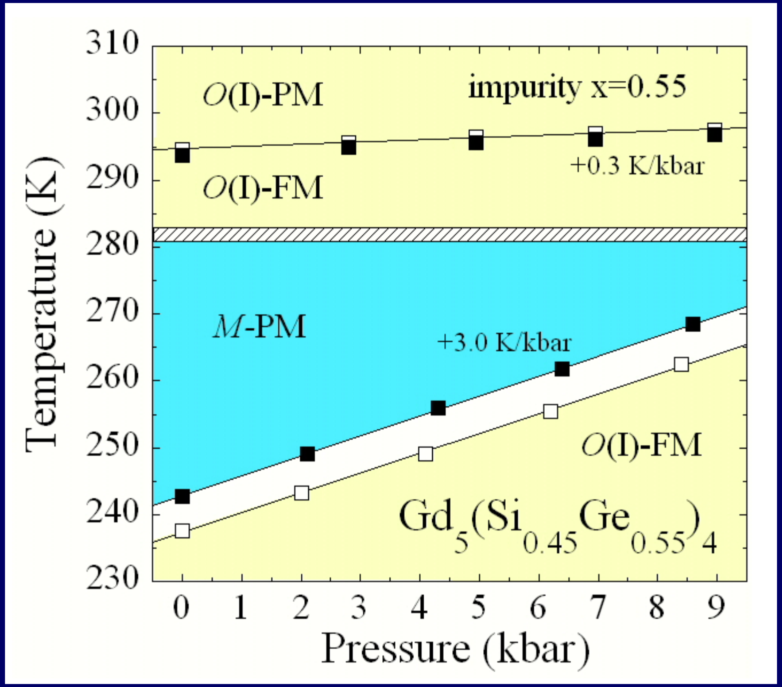
L. Morellon et al, Phys. Rev. B **58**, R14721 (1998)

$Gd_5(Si_xGe_{1-x})_4$ – Hydrostatic Pressure

Pressure dependence of $T_{C/N}$:

- High in Magnetostructural Changes ➡ dT_C/dP=+3.0 K/kbar (x=0.45, 0.1)
- Small in Pure Magnetic Transitions ➡ dT_C/dP=+0.3 K/kbar (x=0.8); dT_N/dP=+0.7 K/kbar (x= 0.1)





Morellon et al., J. Phys.: Condens. Matter **16**, 1623-1630 (2004)

$Gd_5(Si_xGe_{1-x})_4$ - Pressure on polycrystals

VOLUME VS. ELECTRONIC EFFECTS

$$\Gamma = \frac{d \ln T_{C,N}}{d \ln V} = -\frac{1}{\kappa T_{C,N}} \frac{dT_{C,N}}{dP}$$

Γ → from pressure results
($\kappa \approx 1.8$ Mbar^{-1} for all x)

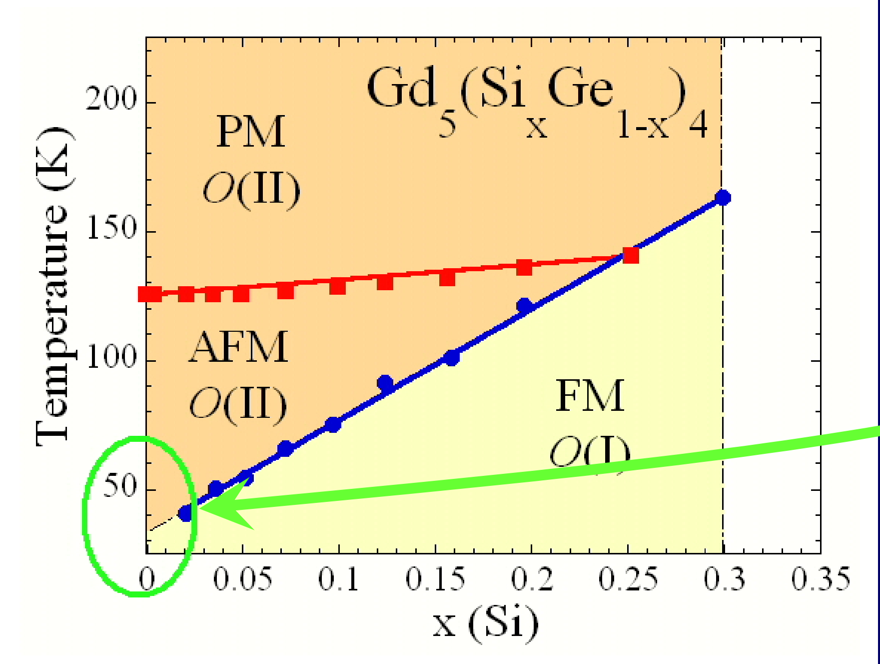
Γ^* → from x-T phase diagram
(cryst. data)

A. O. Pecharsky et al.,
J. All. and Comp. **338** 126 (2002)

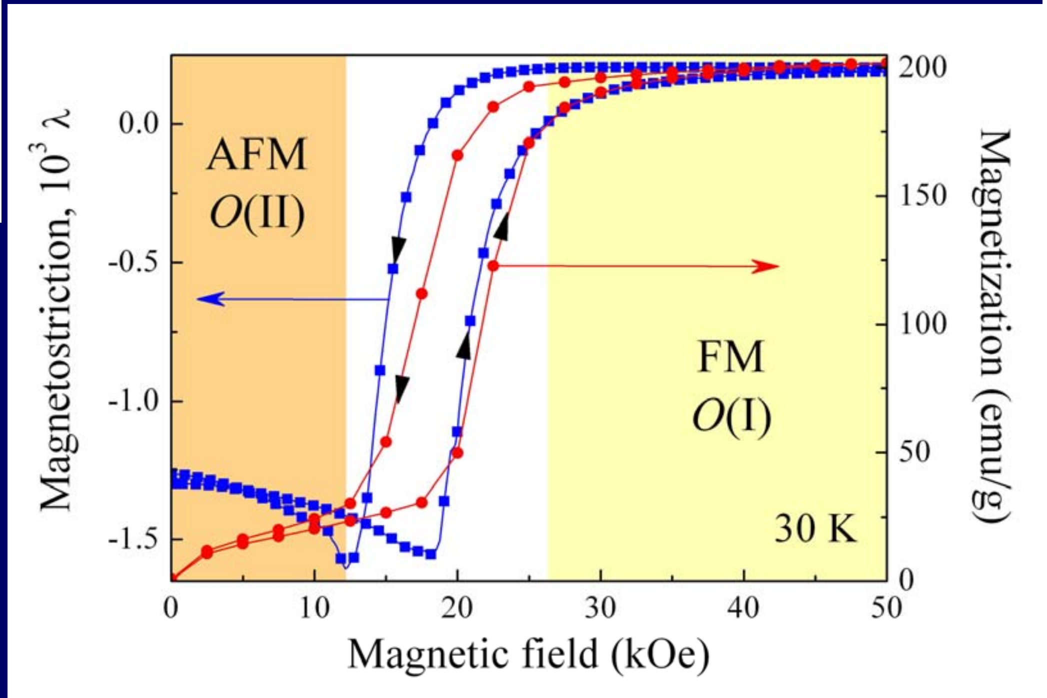
x	Γ	Γ*	Γ*/ Γ
0.8	–0.5	–7	14
0.45	–7	–87	12.4
0.1 (T_C)	–20	–167	8.4
0.1 (T_N)	–3	–14	4.7

$\Gamma^* >> \Gamma$ → Electronic effects are more important ! ! !

Gd_5Ge_4 – Magnetic Field Effects



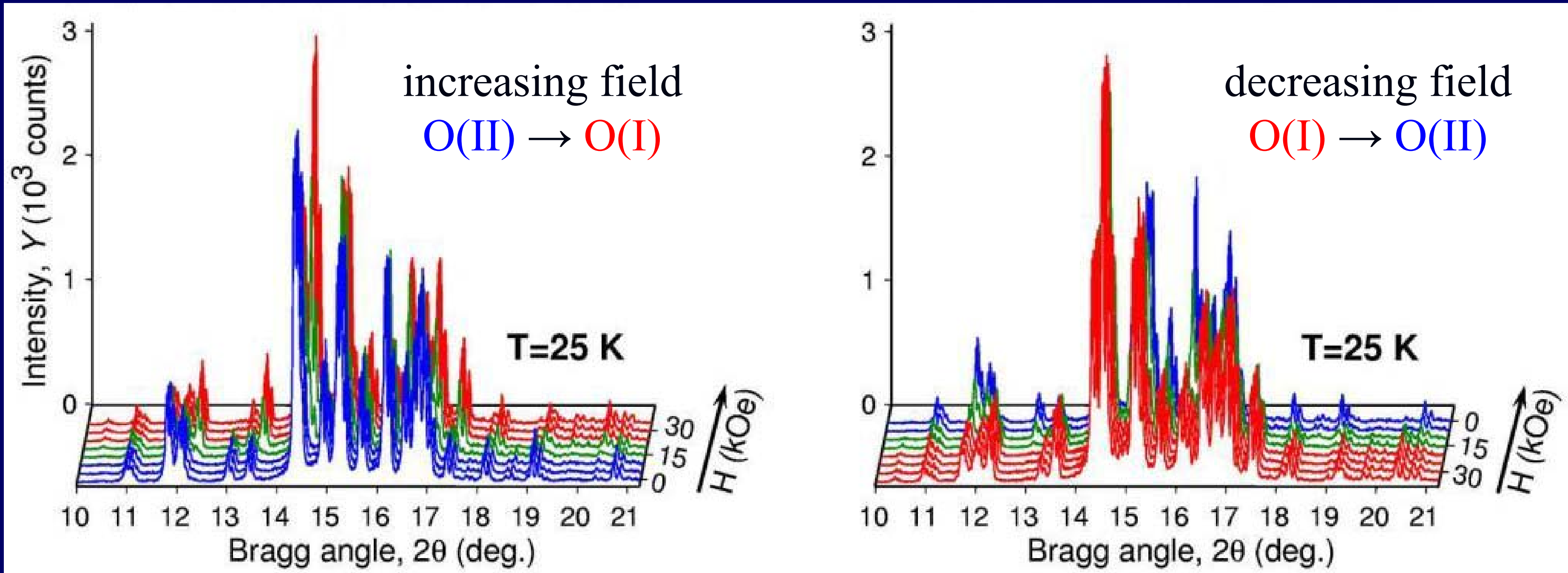
- NO spontaneous (zero-field) low temperature FM ground state



- Magnetic field induced magnetic & structural changes.
- AFM-*O*(II) → FM-*O*(I) transition?

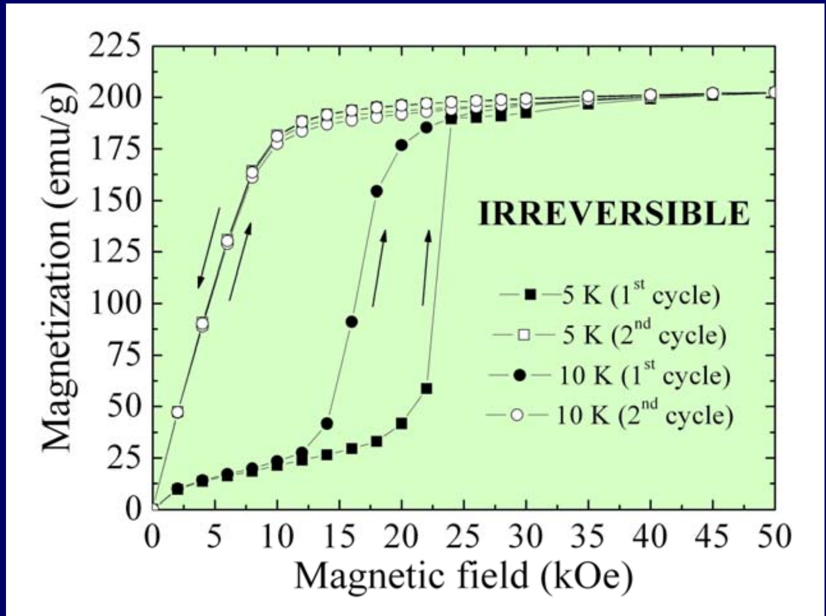
Gd_5Ge_4 – Magnetic Field Effects

- High-resolution **x-ray powder diffraction** up to **H = 35 kOe**.
- First direct **microscopic evidence** of the *O*(II) ↔ *O*(I) **structural transition**.



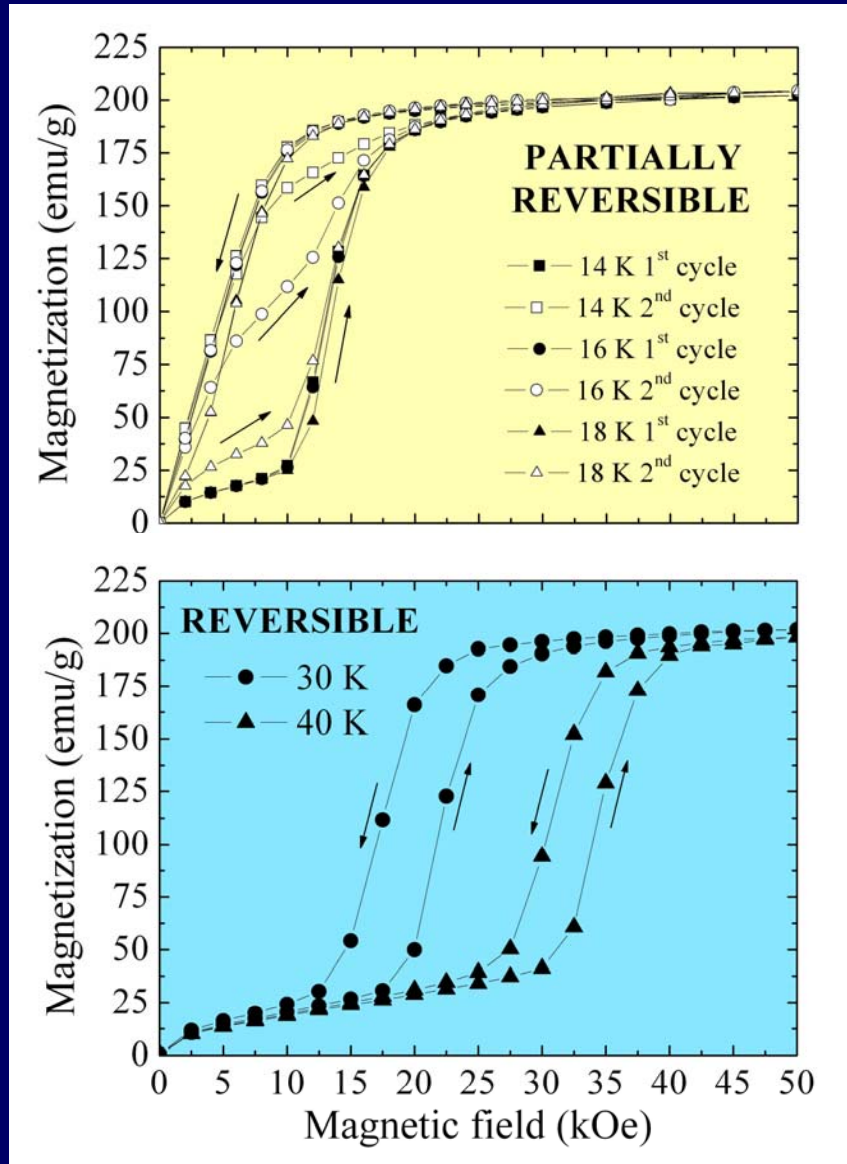
V. K. Pecharsky et al., Phys. Rev. Lett. **91**, 197204 (2004)

Gd_5Ge_4 – Anomalous Magnetic Field Effects

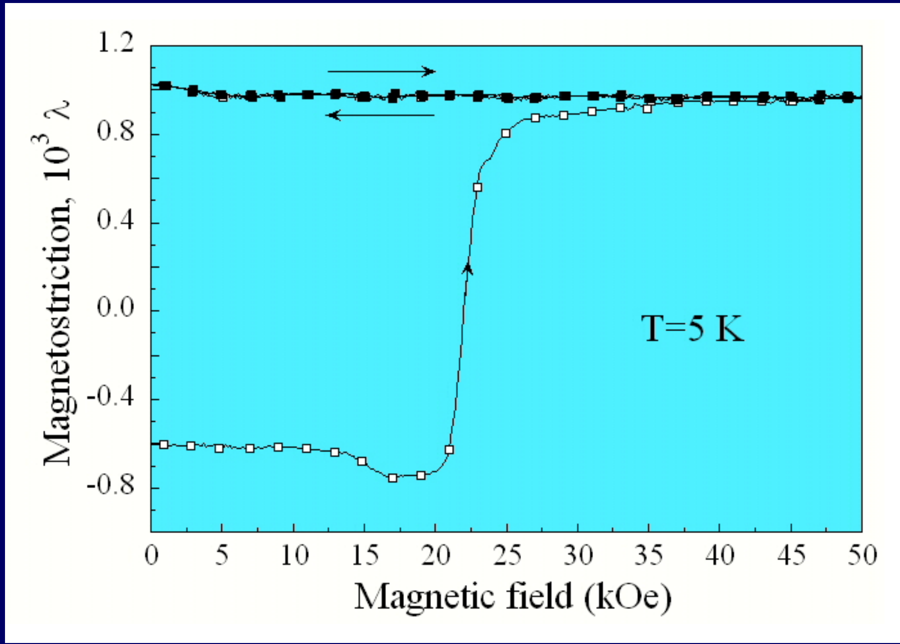


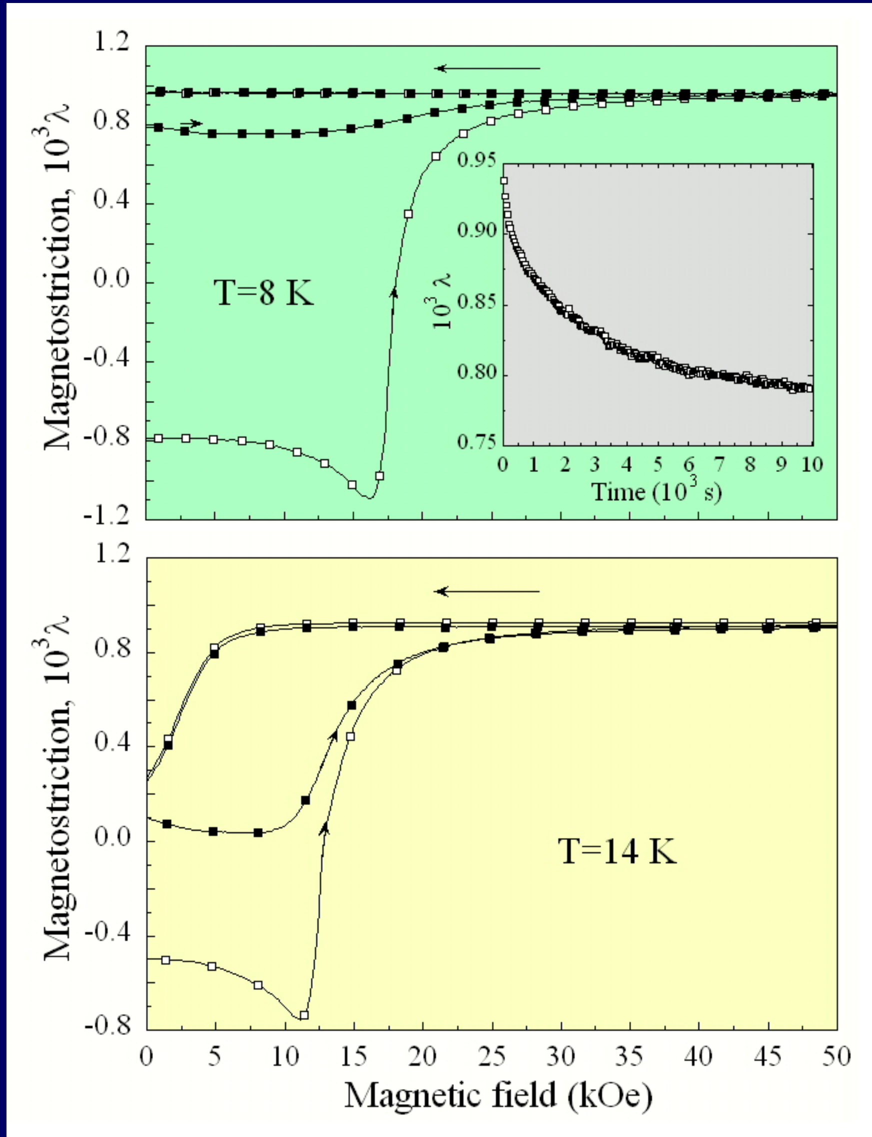
- Field-induced AFM → FM transition…
  - Irreversible at T < 14 K.
  - Partially reversible 14 K ≤ T ≤ 20 K.
  - Reversible T> 20 K

Levin et al., Phys. Rev. B **65**, 214427 (2002)



Gd_5Ge_4 – Anomalous Magnetic Field Effects





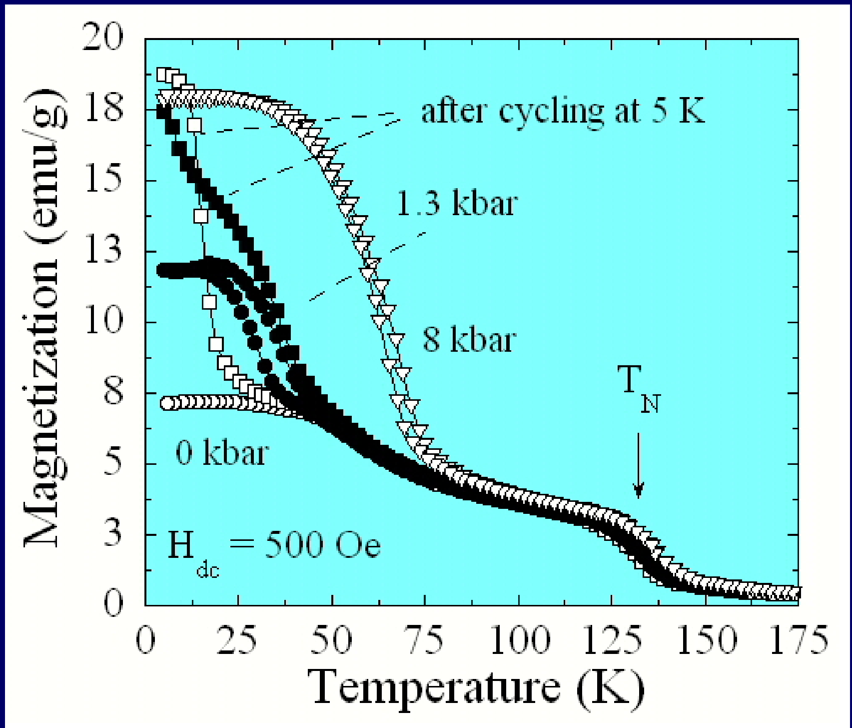
- Field-induced *O*(II) → *O*(I) transition:
  - Irreversible at T < 8 K
  - Partially reversible 8 K < T < 20 K
  - Reversible T > 20 K

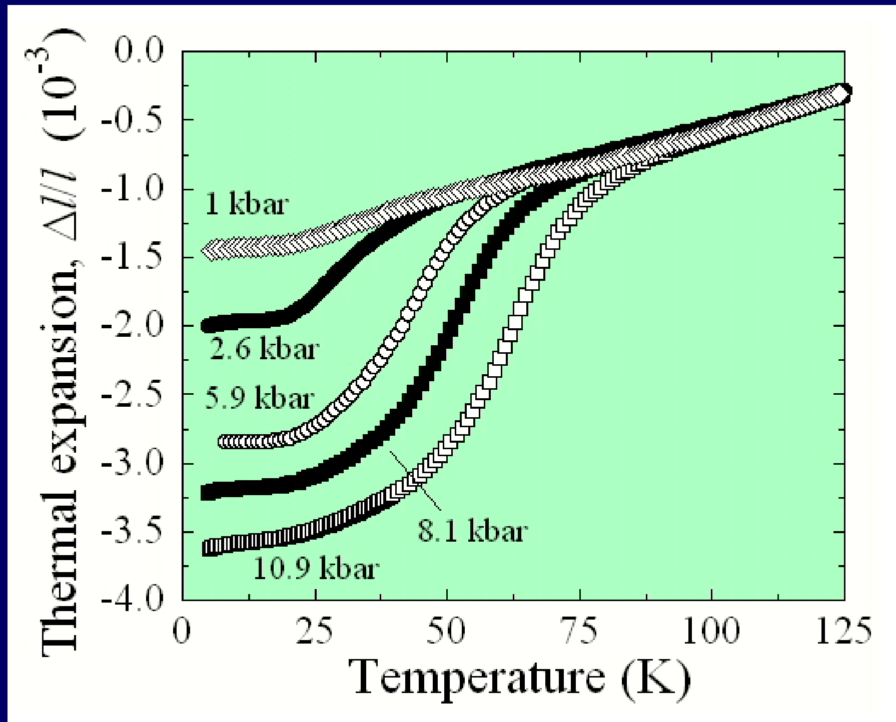
Magen et al., J. Phys:.Condens Matter **15**, 2389 (2003)

Gd_5Ge_4 – Pressure induced *O*(I)-FM State

► Pressure induced anomalies at low temperature:

- Rise of magnetic signal (FM?) with "T_C" increasing with pressure.
- Onset of LTE anomaly increasing in size and temperature with pressure.





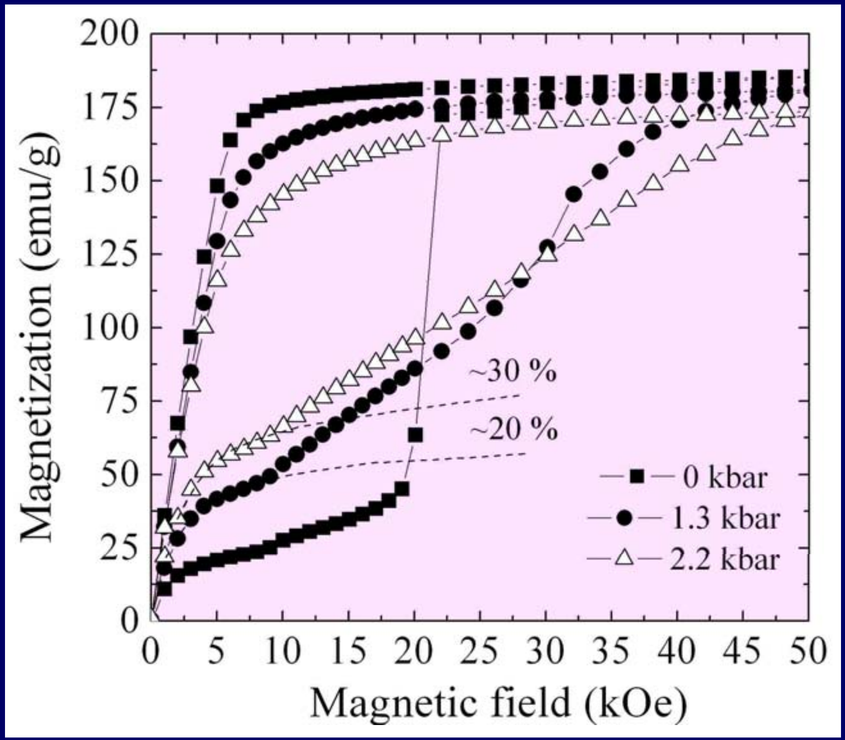
Magen et al., Phys. Rev. Lett. **91**, 207202 (2003).

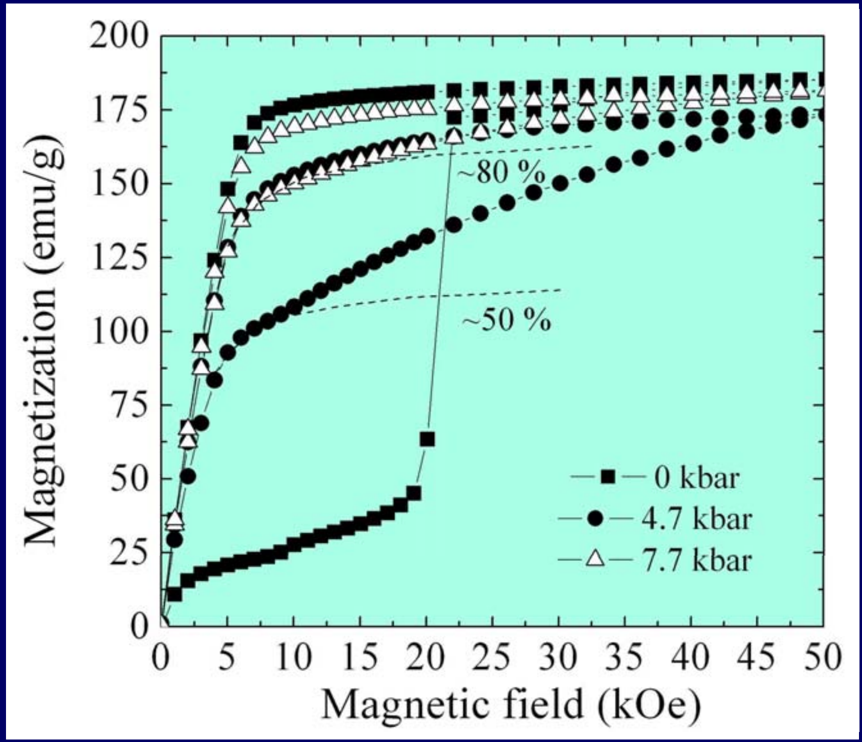
Gd_5Ge_4 – Pressure-induced *O*(I)-FM State

► Magnetization isotherms:

● Progressive increase of a FM component.

● Estimation of a volume of FM regions considering 100% FM at 11 kbar.



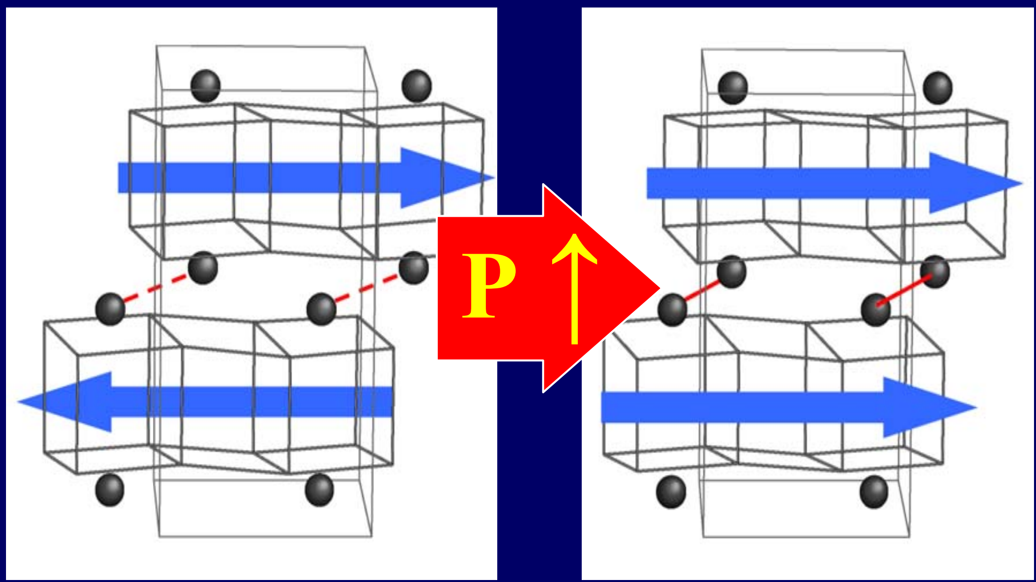


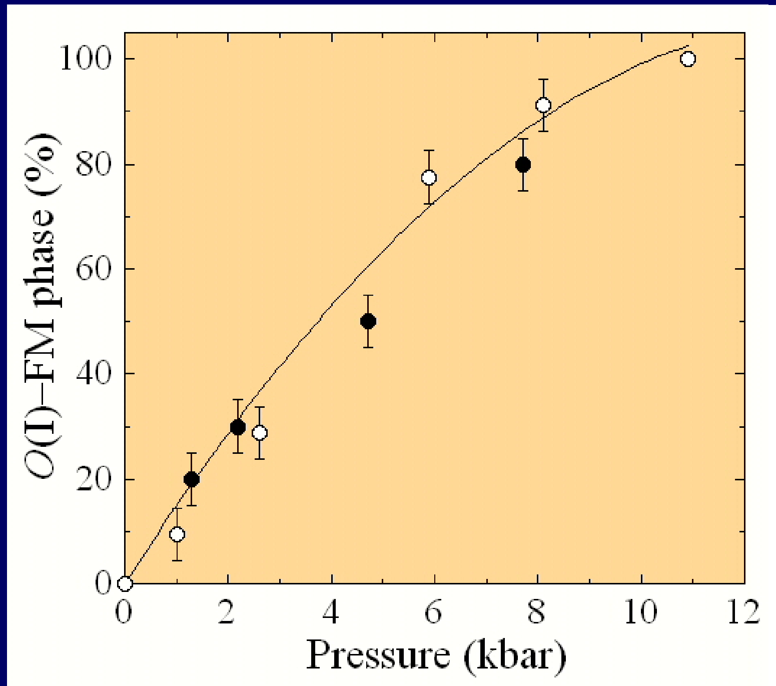
Magen et al., Phys. Rev. Lett. **91**, 207202 (2003).

Gd_5Ge_4 – Pressure-induced *O*(I)-FM State

► Phase segregation induced by hydrostatic pressure:

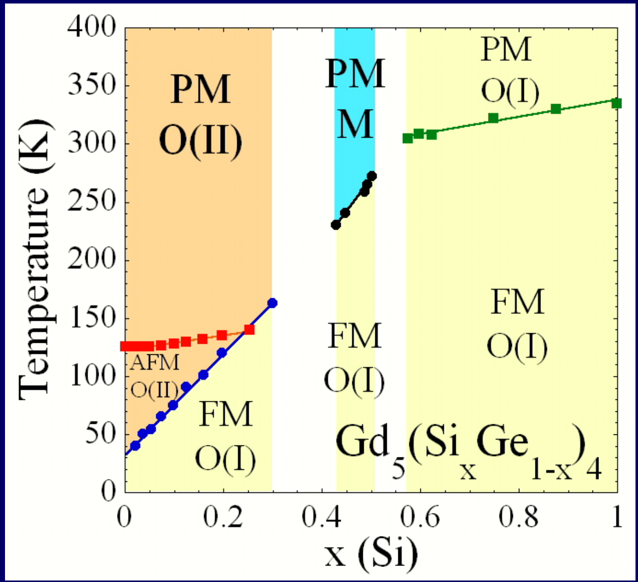
- *O*(II)-AFM → *O*(II)-AFM + *O*(I)-FM → *O*(I)-FM.
- 100 % of *O*(I)-FM at P ≈ 10 kbar.

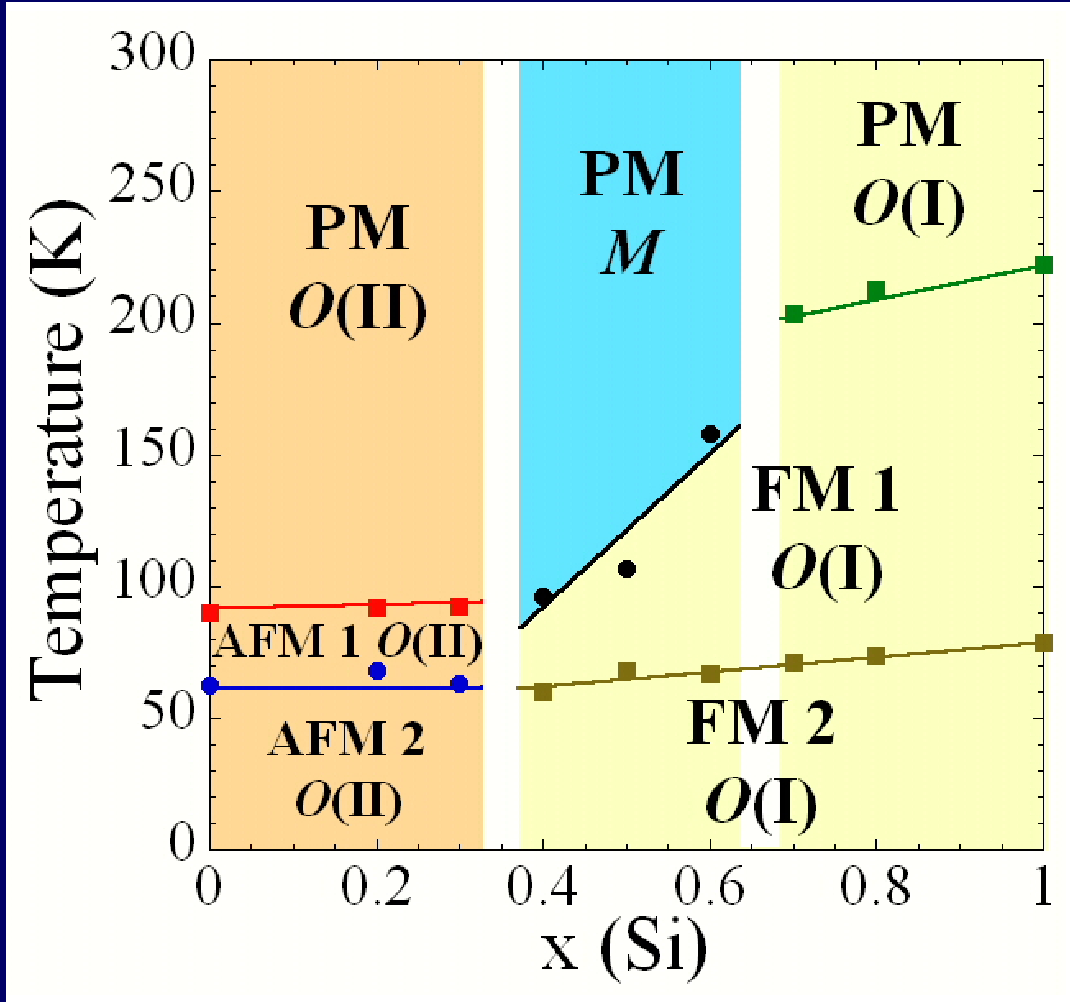




Magen et al., Phys. Rev. Lett. **91**, 207202 (2003).

$Tb_5(Si_xGe_{1-x})_4$ – x-T Phase Diagram





- The same crystal structures
- Transitions shifted to lower T
- Wealth of magnetic structures

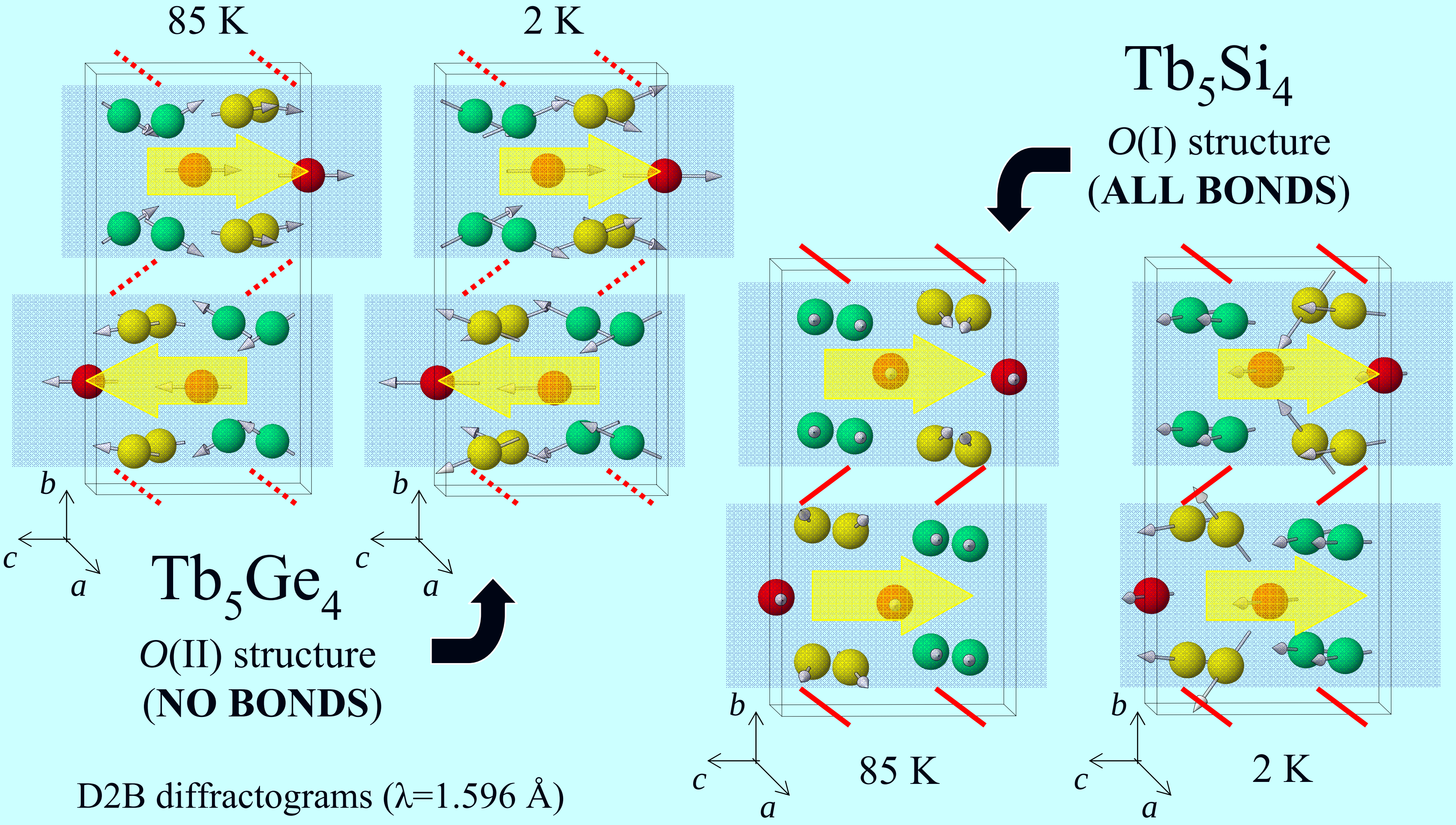
New transitions:

FM1 ↔ FM2 [in O(I)]

AFM1 ↔ AFM2 [in O(II)]

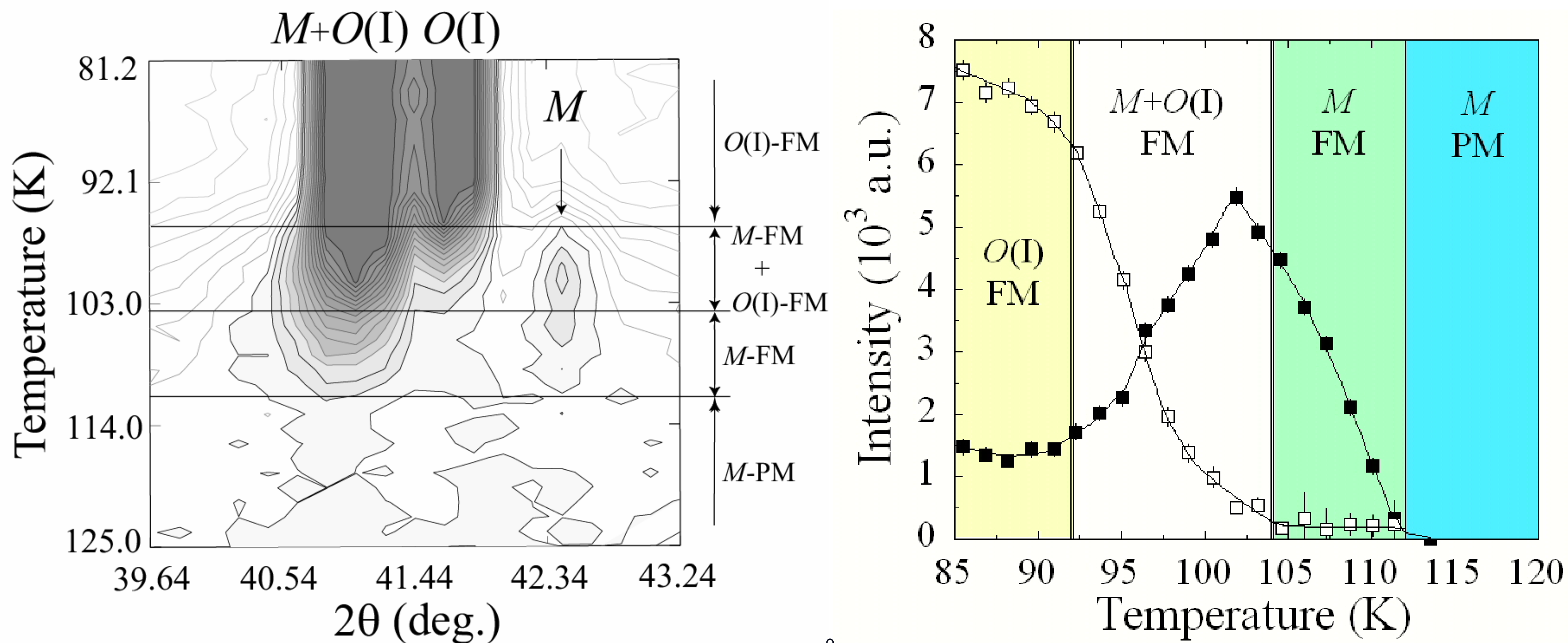
C. Ritter et al., Phys. Rev. B **65**, 094405 (2002).

$Tb_5(Si_xGe_{1-x})_4$ – x-T Phase Diagram



C. Ritter et al., Phys. Rev. B **65**, 094405 (2002).

$Tb_5Si_2Ge_2$ – Decoupling of magn. & struc.



D1B scan (λ=2.52 Å), magnetic peaks

- No coupled *M*-PM ↔ *O*(I)-FM transition takes places.
- A new intermediate *M*-FM phase grows in the 105-115 K.

Morellon et al., Phys. Rev. B **68**, 024417 (2003)

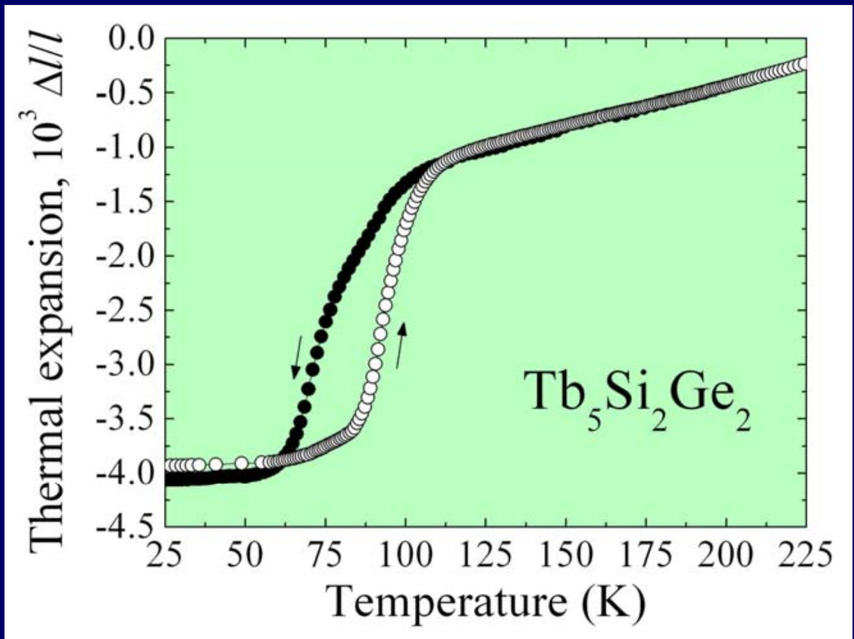
$Tb_5Si_2Ge_2$ – Field-induced transition?

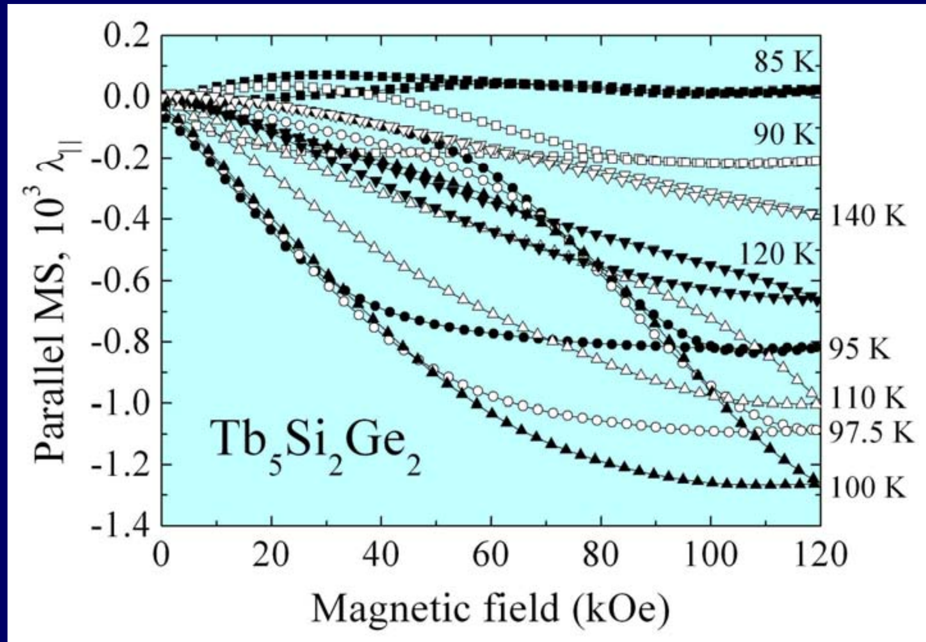
- Disagreement → temperature ≠ field induced transformations.

  Examples: LTE/MS, transport measurements.

$$\Delta L/L \approx +0.26\ \% \quad \neq \quad MS_{max} \approx +0.12\ \%$$

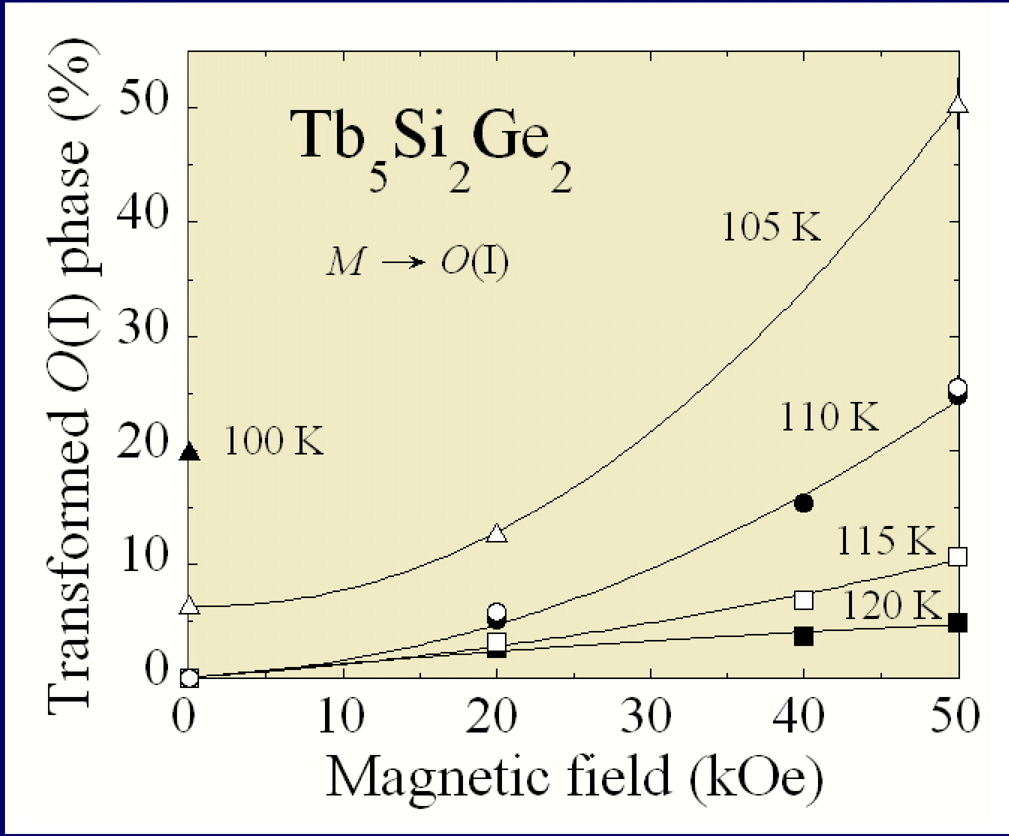
$$\Delta R/R \approx -30\ \% \quad \neq \quad MR_{max} \approx -14\ \%$$





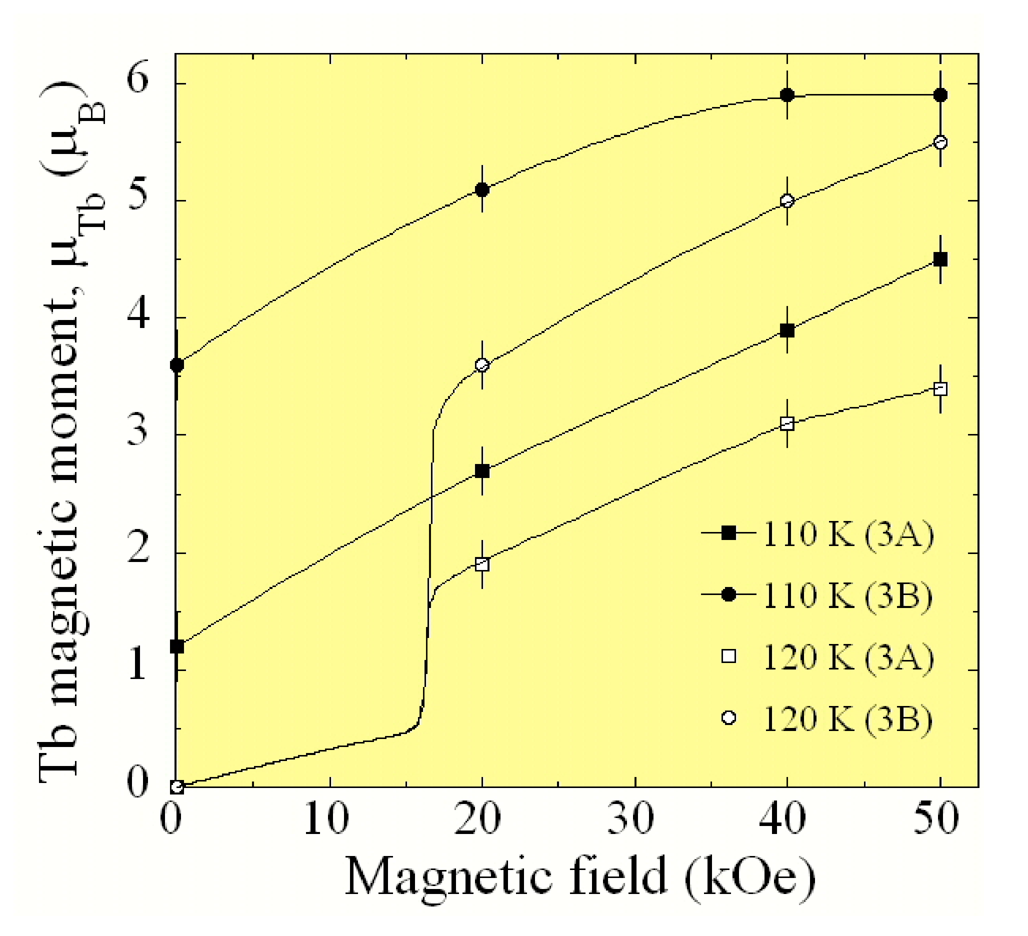
$Tb_5Si_2Ge_2$ – Field-induced transition?

- Incomplete $M \leftrightarrow O$(I) transition, max. 50 % O(I)-FM. X-ray vs. High Field?
- Inefficient magnetic field in PM, need for FM in M phase.



D2B diffractograms vs. H (λ=2.398 Å)

$Tb_5Si_2Ge_2$ – Field-induced transition?



- Tb 3A – near the bonds
- Tb 3B – near the broken pairs
- μ_{Tb3A}'s > μ_{Tb3B}'s
- The existence of T′-T′ bonds enhances the FM interactions (higher magnetic moments)
- T=120 K (*M* phase):
  Low-field: PM
  High-field: FM

Field-induced FM ordering in the *M* phase!

D2B diffractograms vs. H (λ=2.398 Å)

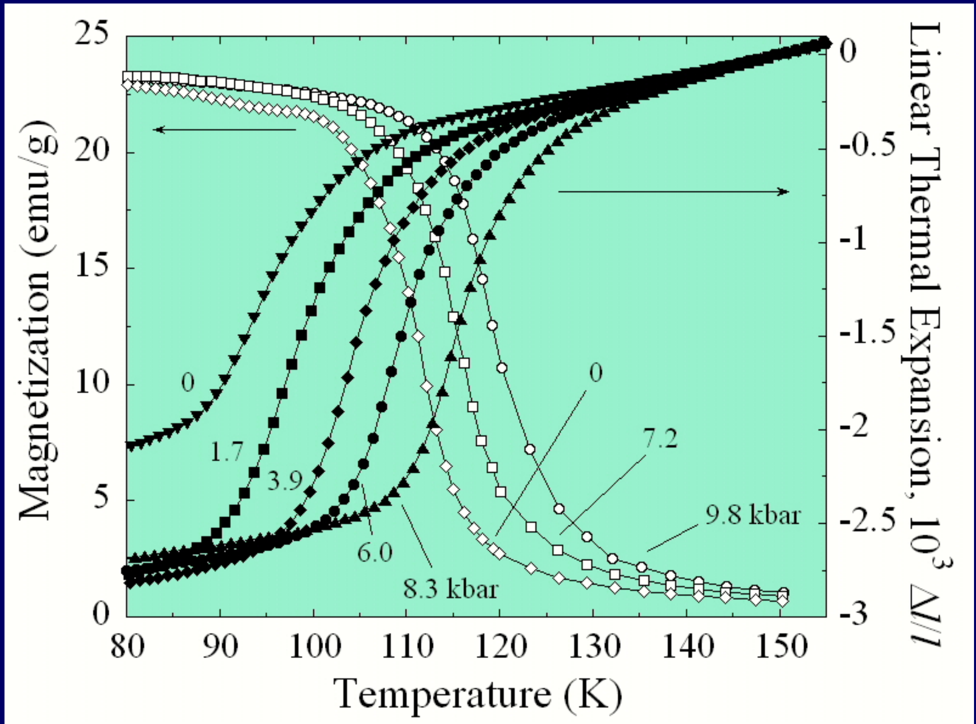
$Tb_5Si_2Ge_2$ – Decoupling, but… ?

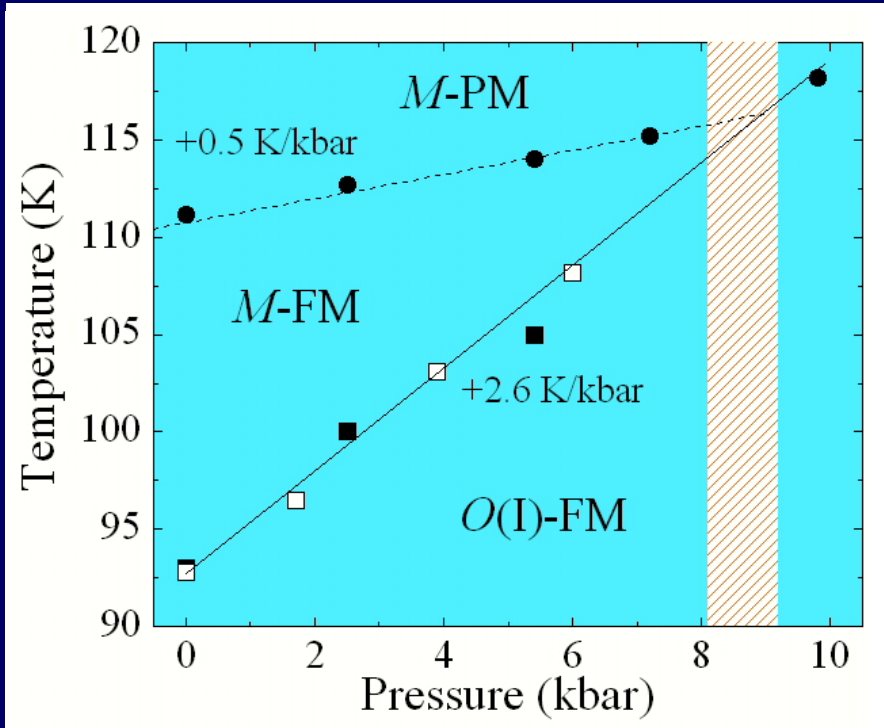
► Remember $Gd_5(Si_xGe_{1-x})_4$!

● Magnetic anomalies – low P dependence $dT_C/dP \approx +0.3\text{-}0.7$ K/kbar

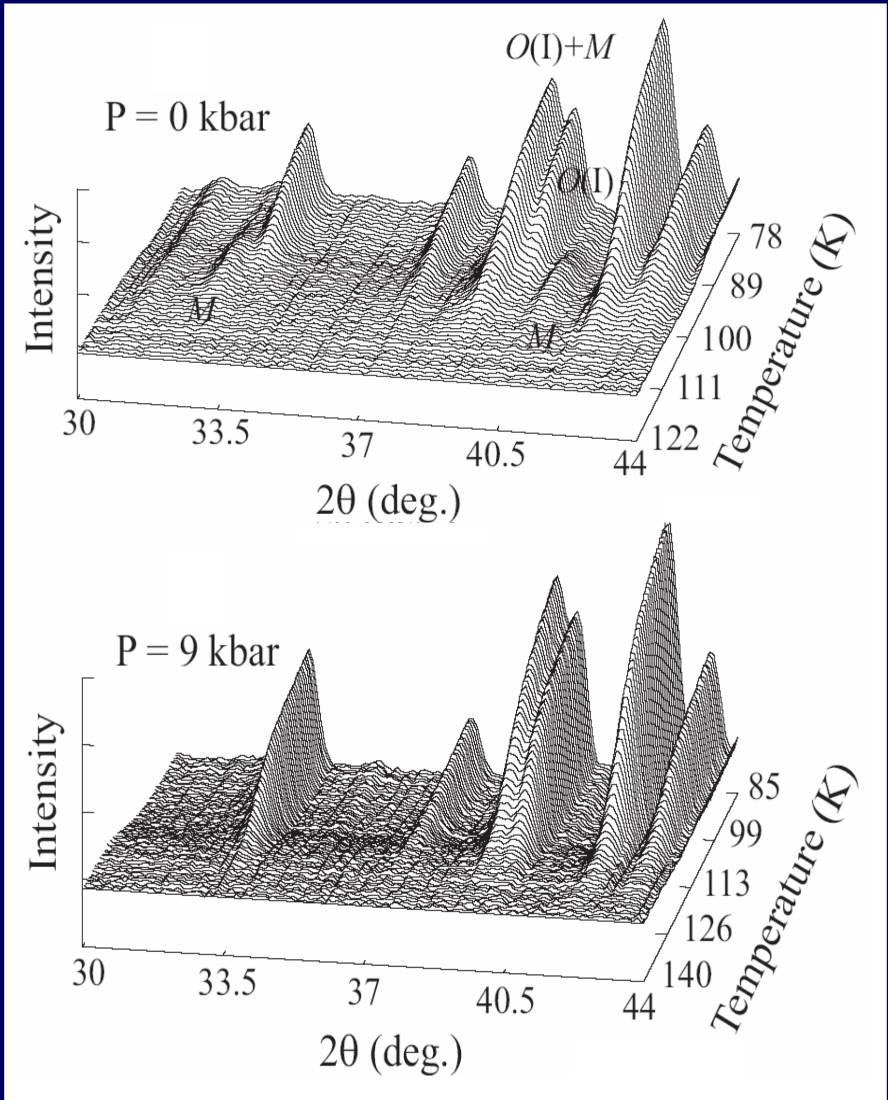
● Structural anomalies – high P rate $dT_C/dP \approx +3.0$ K/kbar

► Is it the same in $Tb_5Si_2Ge_2$? Could we merge both anomalies?





$Tb_5Si_2Ge_2$ – … Pressure kills *M*-FM!



D20 thermal scans vs. P (λ=2.4 Å)
Magnetic peaks

Upon increasing pressure…

- *M* magnetic peaks disappear
- All peaks [*O*(I)] grow together

► Pressure-induced recoupling of the crystal and magnetic changes & destruction of the *M*-FM phase

$Tb_5Si_2Ge_2$ – Pressure enhancement of MCE

Recoupling of the structural and magnetic transitions/entropy changes!!! → Enhancement of the MCE
Onset of GMCE

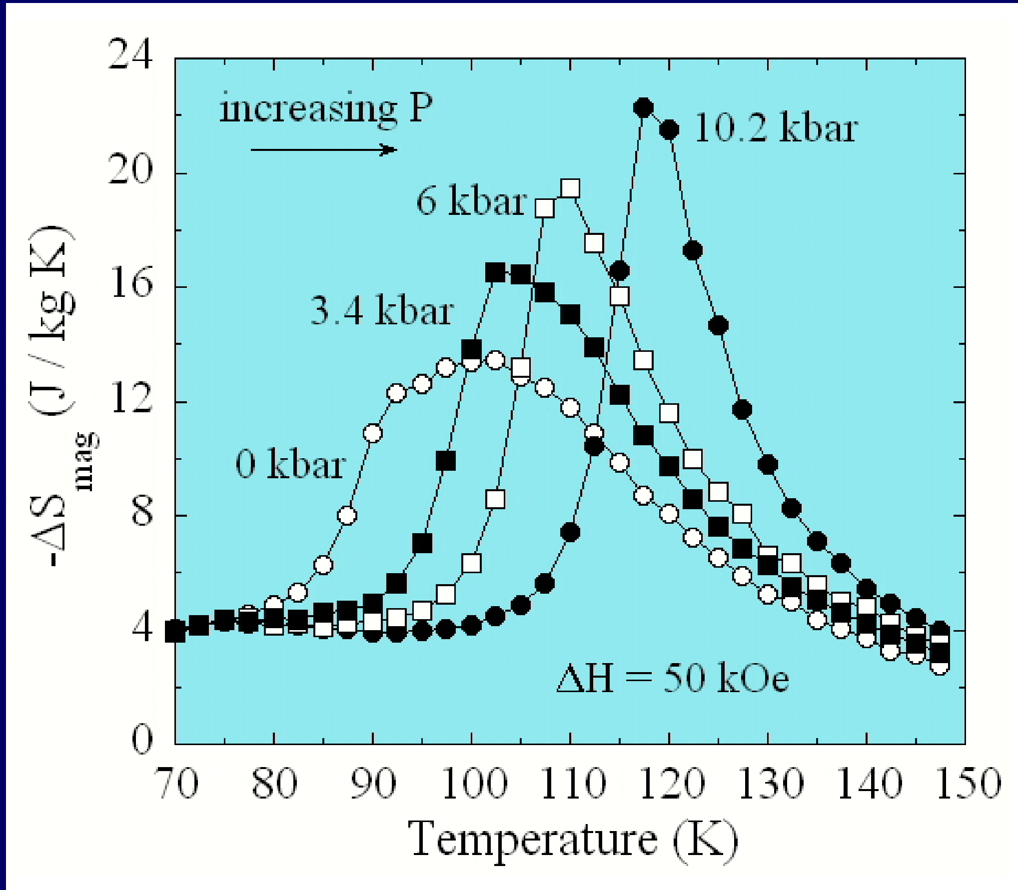
- Calculation of the MCE

$$\Delta S_M = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_H dH$$

- Contributions to the MCE:

$$\Delta S_M = \Delta S_{mag} + \Delta S_{str}$$

Morellon et al.
Phys. Rev. Lett. **93**, 137201 (2004).



$Tb_5Si_2Ge_2$ – Griffiths-like behavior in *M*-PM

► **What's A Griffiths Phase (GP)?** $T_C < T < T_G$ (T_G = Griffiths temp.)

THEORY: **Non-analytical** thermodynamical functions.

MICROSCOPIC INGREDIENTS:

- **Randomly** distributed magnetic interactions (**disorder**).
- **Phase coexistence** phenomena.
- **Competition** between magnetic **interactions:**
  e.g., FM double exchange – AFM superexchange, Kondo vs. RKKY.
- Others: magnetic anisotropy, intrinsic disorder.

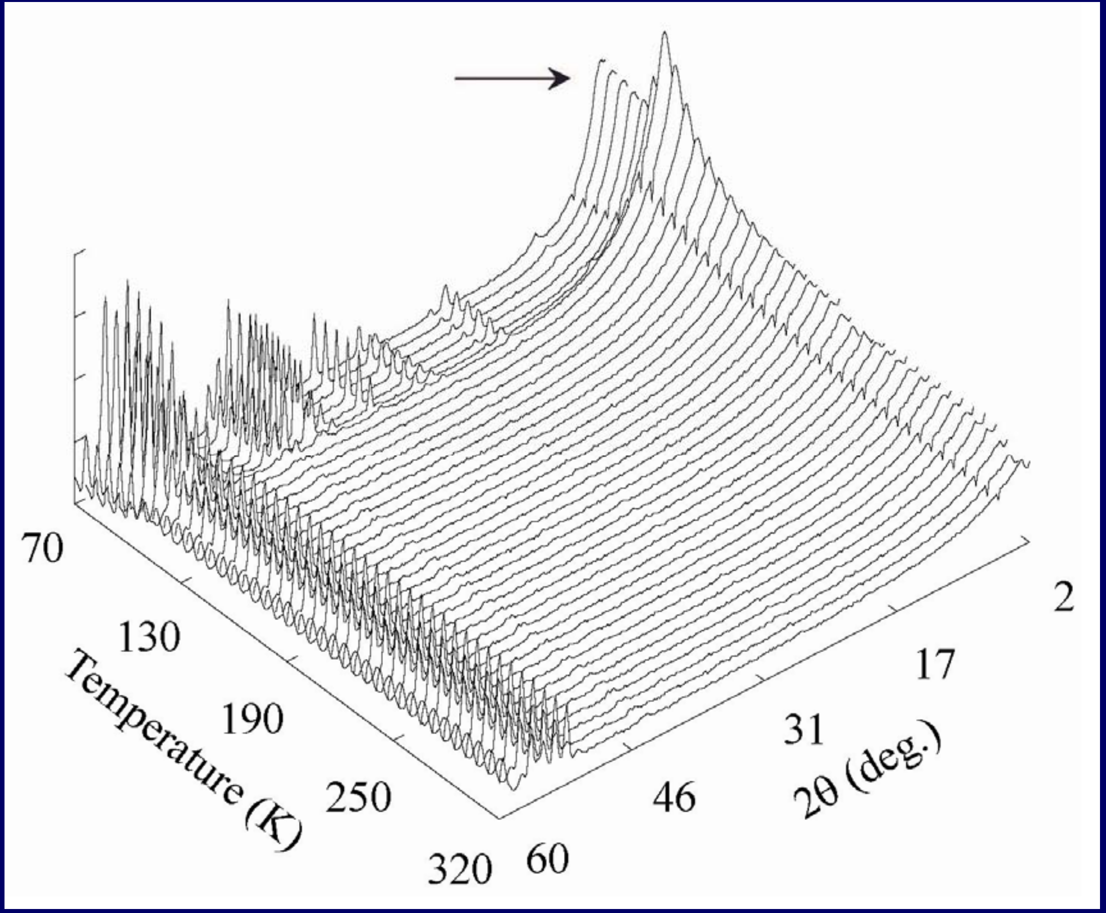
MACROSCOPIC ANOMALIES:

e.g. **cluster-like** behavior in **magnetic susceptibility**.

$$\chi^{-1} \propto (T - T_C)^{1-\lambda}, \quad 0 < \lambda < 1$$

$Tb_5Si_2Ge_2$ – GP-like behavior in *M*-PM

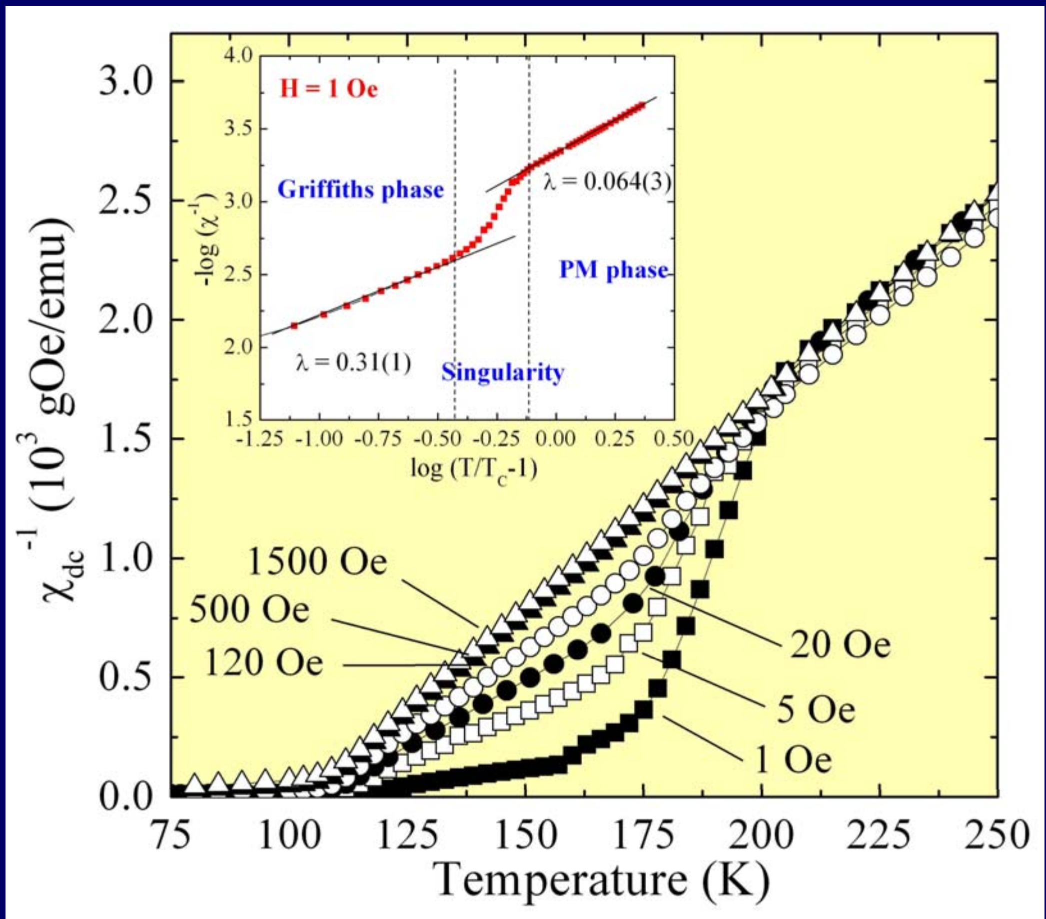
- Anomalous SANS contribution at $T > T_C$ in $\theta < \theta_{Bragg}$



D1B temperature scan (λ=2.52 Å)

$Tb_5Si_2Ge_2$ – GP-like behavior in *M*-PM

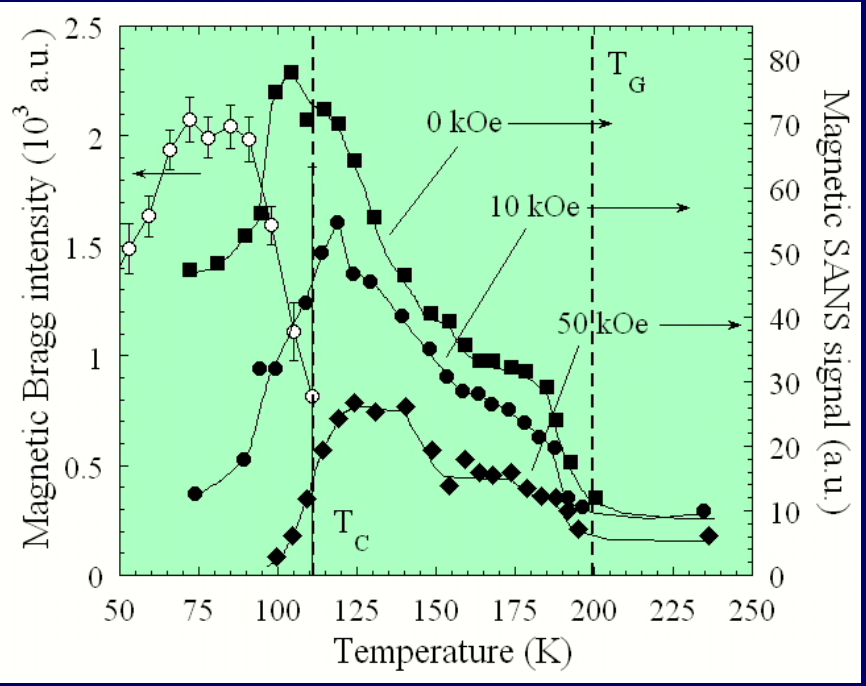
- High spin entities at 110 K < T < 200 K in low field (μ_{eff}>9.72μ_{eff}/Tb).
- GP behavior ↔ λ ~ 0.3 in 125 K < T < 165 K.

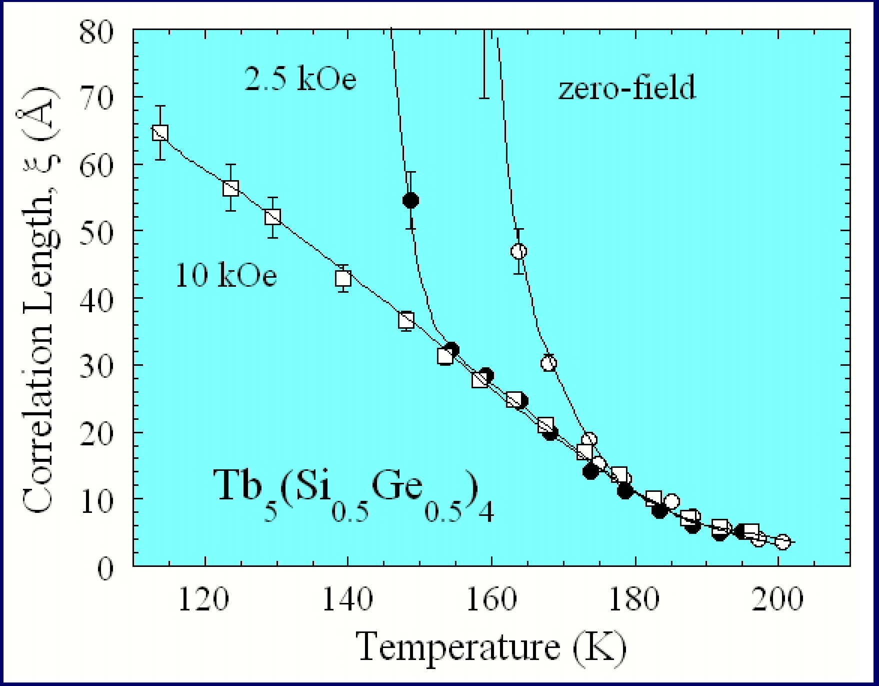


Magen et al.
Phys. Rev. Lett. **96**, 167201 (2006).

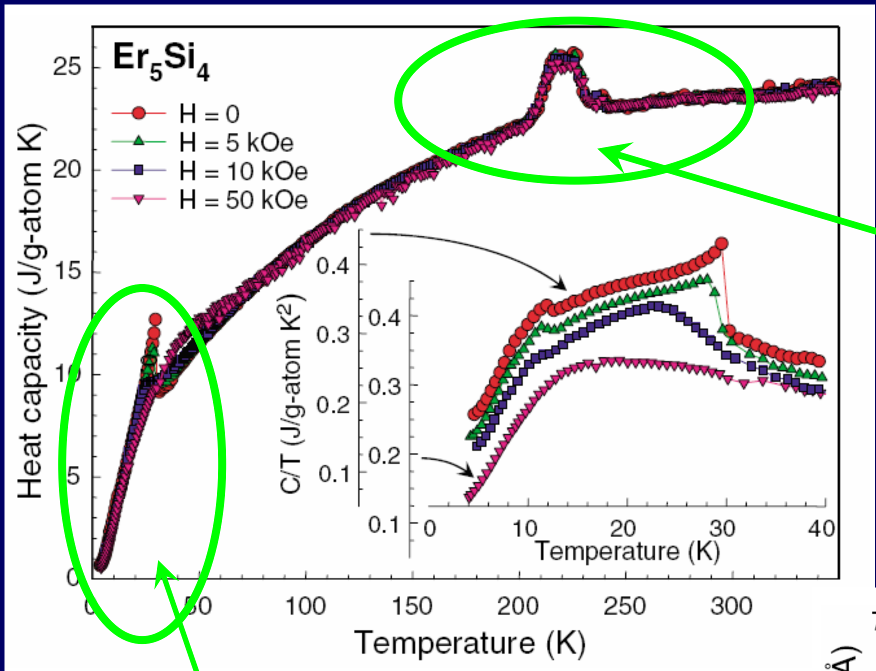
$Tb_5Si_2Ge_2$ – GP-like behavior in *M*-PM

- Increasing magnetic field:
  - Decrease of I_{SANS} (scattering centers)
  - Divergence of ξ at lower T's
- ξ saturates at $H \approx$ 5-10 kOe
- $T_G \approx 200$ K $\approx T_C$ of Si-rich O(I) → Posible *O*(I) character? X-ray vs. Field!





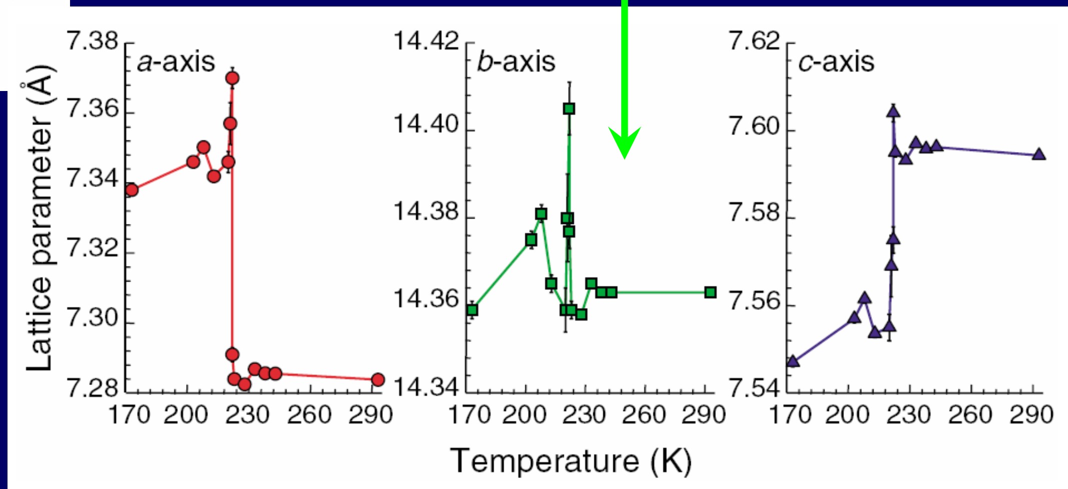
Er_5Si_4 – A new way of decoupling



High-temperature structural transformation on cooling O(I) → M

Inverse order of the phases!

Low-T FM ordering (FM, …also M ?)

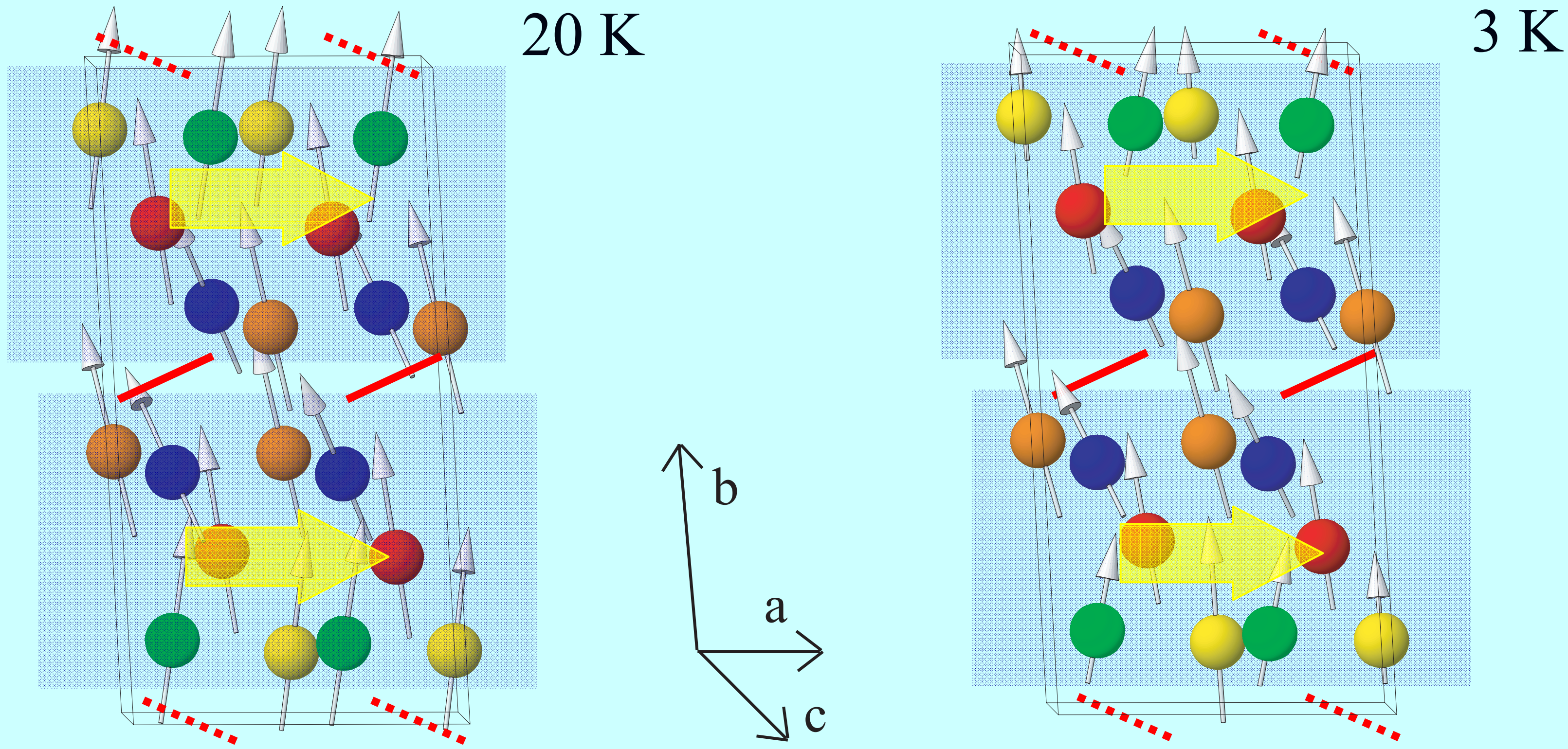


V. K. Pecharsky et al. Phys. Rev. Lett. **91**, 207205 (2004)

Er_5Si_4 – Magnetic Structure

- Net FM component along *b* + small AFM canting in the (010) plane
- Low temperature *M*-FM structure & Spin Reorientation at T ≈ 15 K

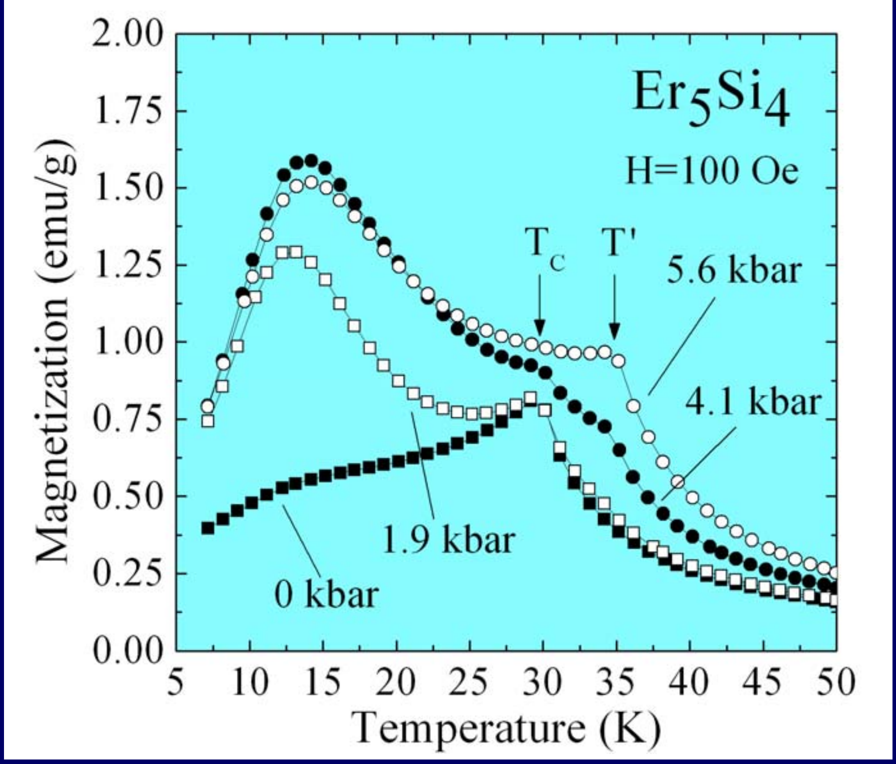
D2B diffractograms (λ=1.596 Å)

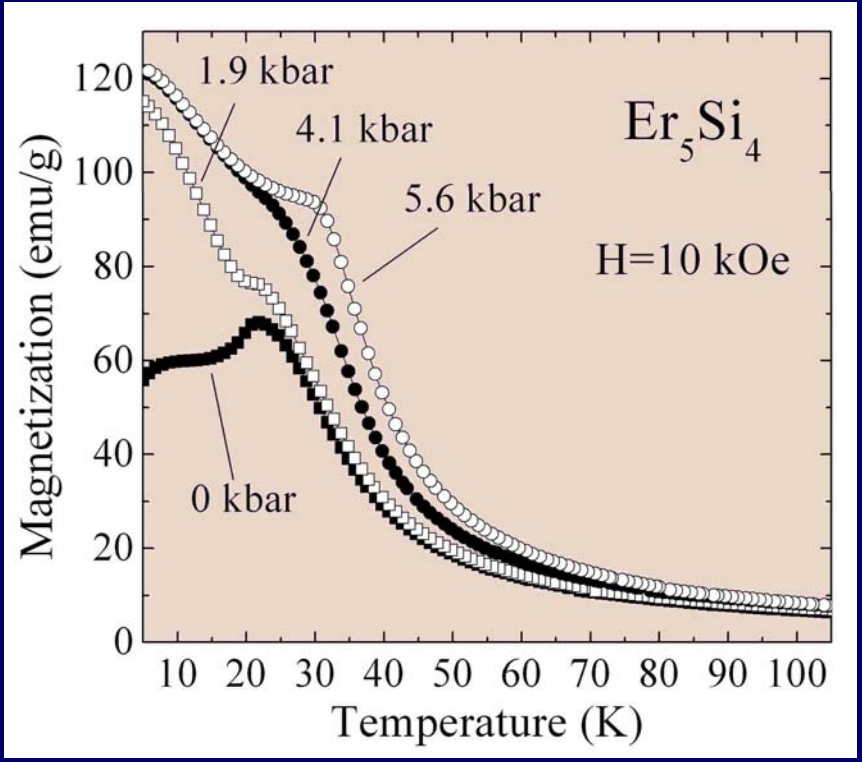


C. Ritter et al., J. Phys.: Condens. Matter. **18**, 3937 (2006).

Er_5Si_4 – Astonishing pressure effects (M)

- P-induced rise of magnetization below T_C (FM→FM' transition?).
- Rise of ordering temperature changes from T_C=30 K to T′=35 K

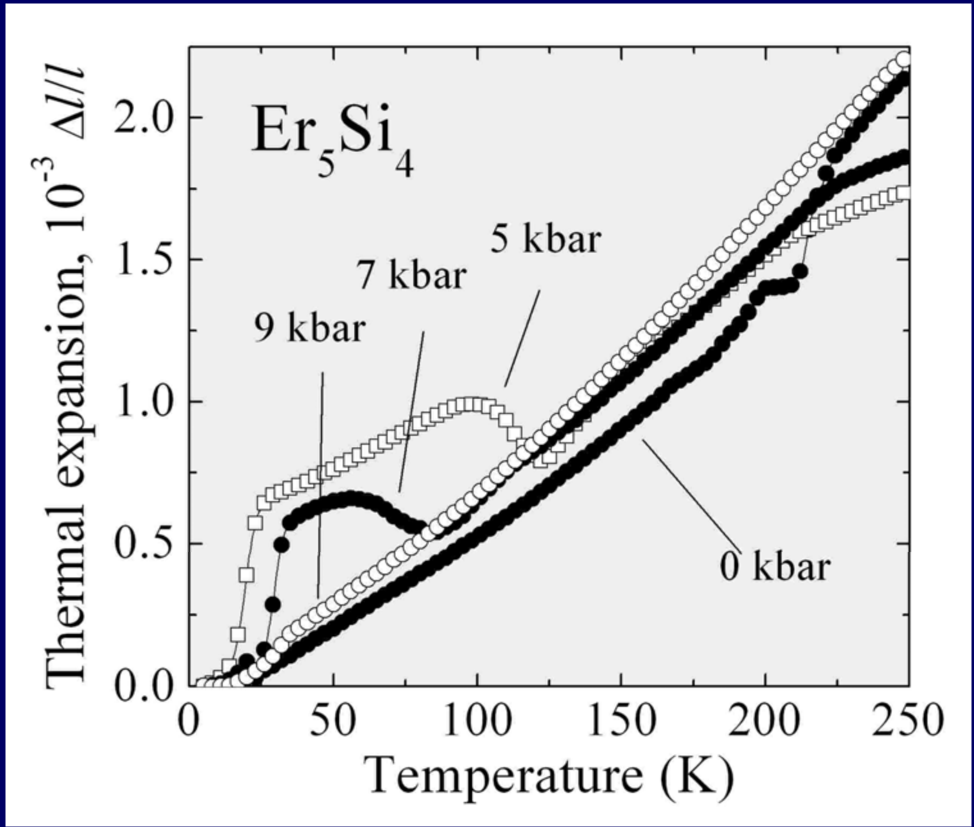




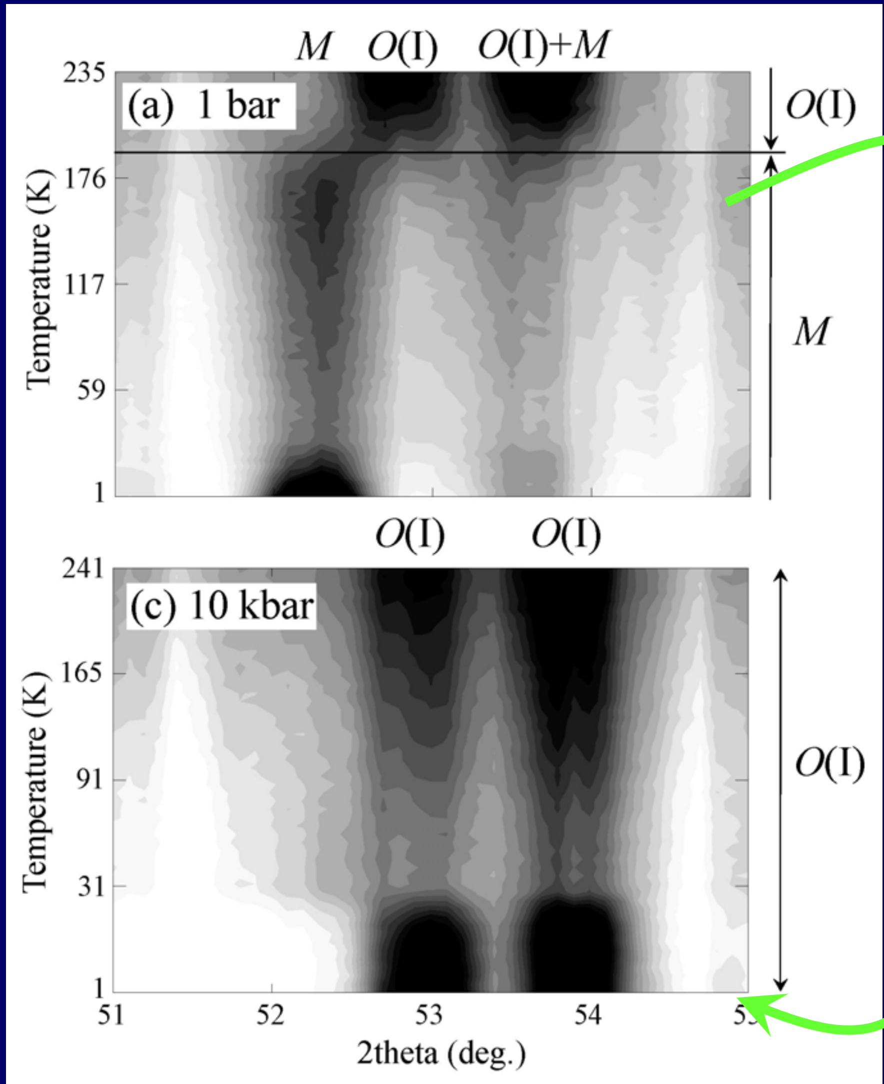
Magen et al., Phys. Rev. B **74**, 134427 (2006).

Er_5Si_4 – Astonishing pressure effects (LTE)

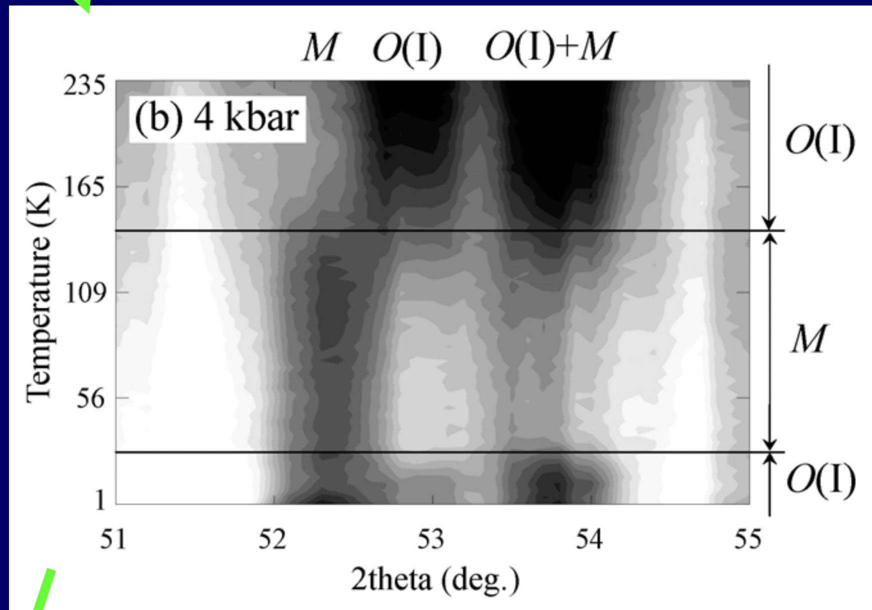
- *O*(I) ↔ *M* transition rapidly shifted to low temperature.
- Inverse structural change appears below T_C.
- Both anomalies kill each other below 9 kbar



Er_5Si_4 – Astonishing pressure effects (neutrons)



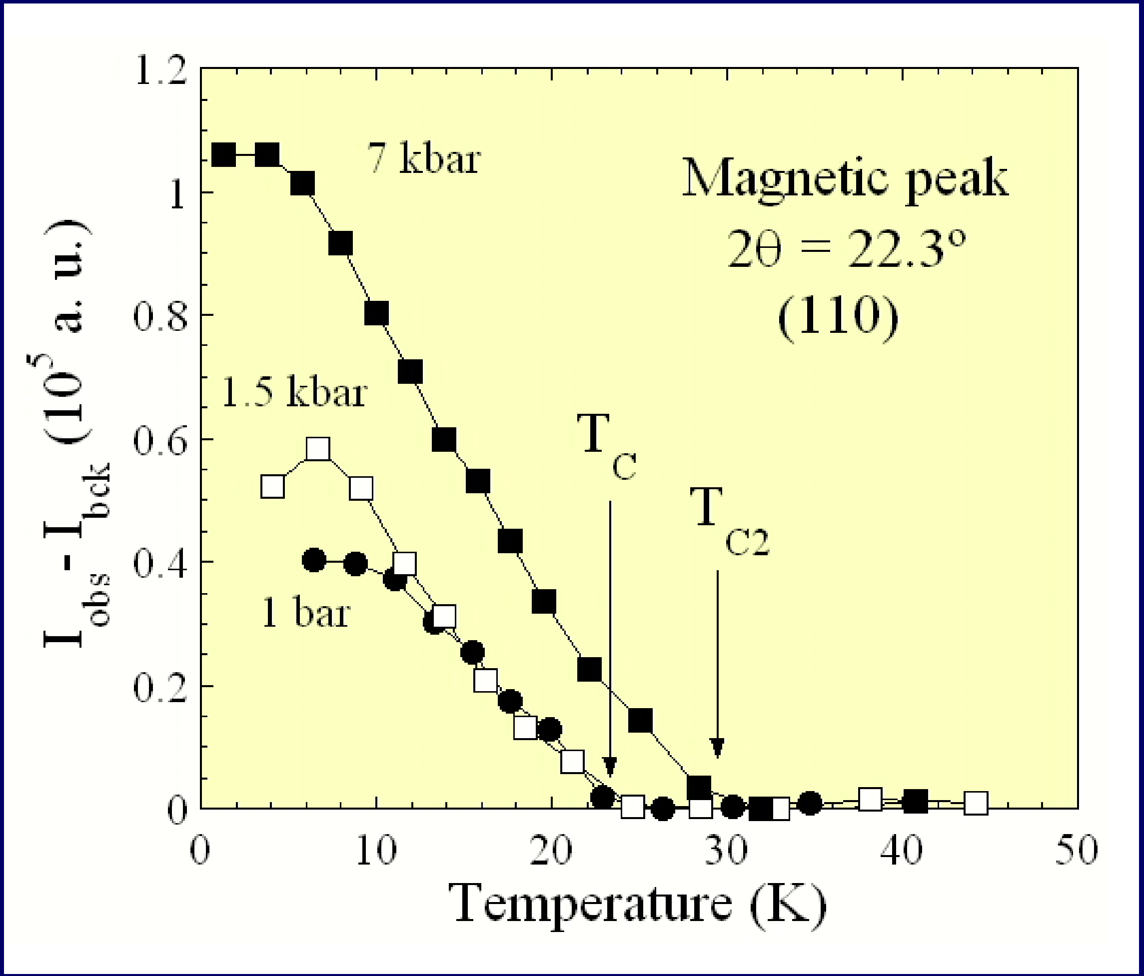
D20 diffractograms vs T, P



- Neutrons confirm LTE behavior.

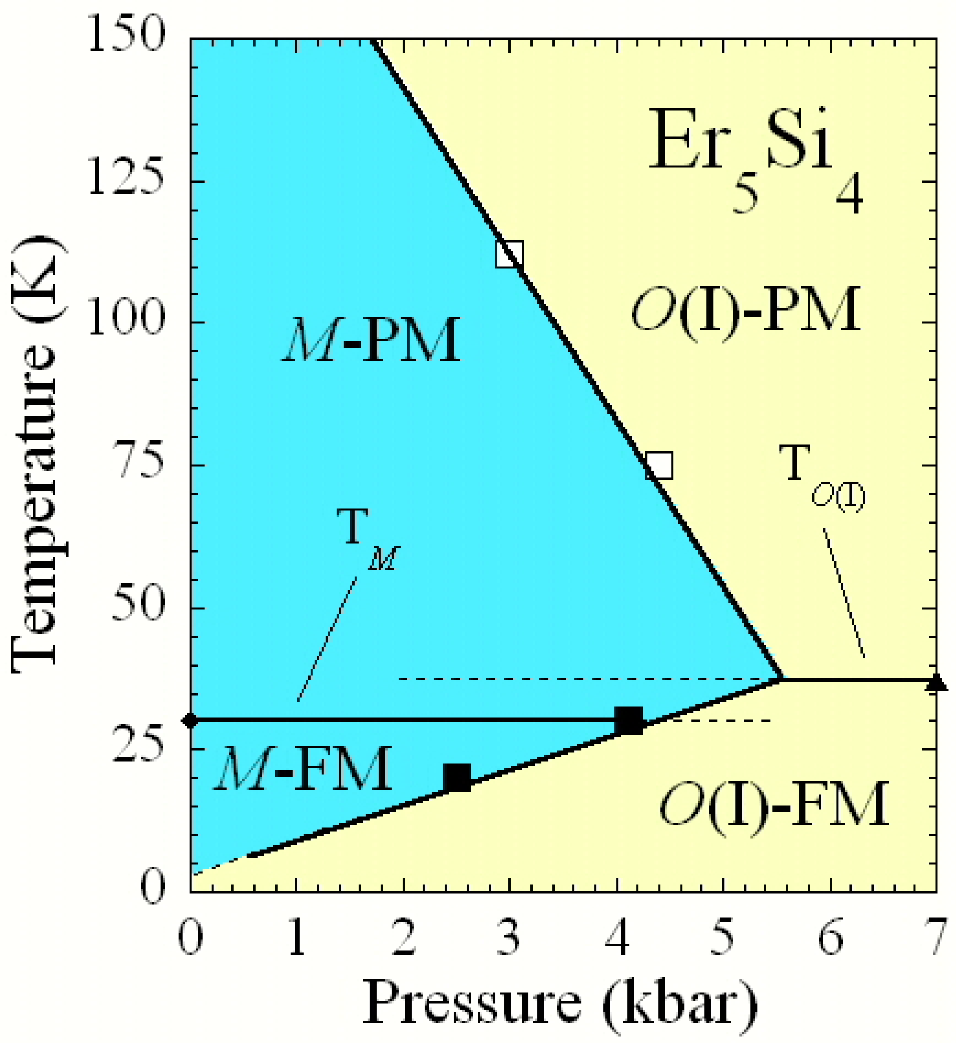
Er_5Si_4 – Astonishing pressure effects (neutrons)

- Neutrons confirm magnetization behavior → T_{C2} [O(I)] > T_{C1} [M]



D20 diffractograms vs T, P

Er_5Si_4 - T-P phase diagram



- Rapid *O*(I) → *M* (high T)

  $dT_{t1}/dP \approx -23\text{-}30$ K/kbar

- Slow *M* → *O*(I) (low T)

  $dT_{t2}/dP \approx +6$ K/kbar

- P > 5.5 kbar, *O*(I) at all T's

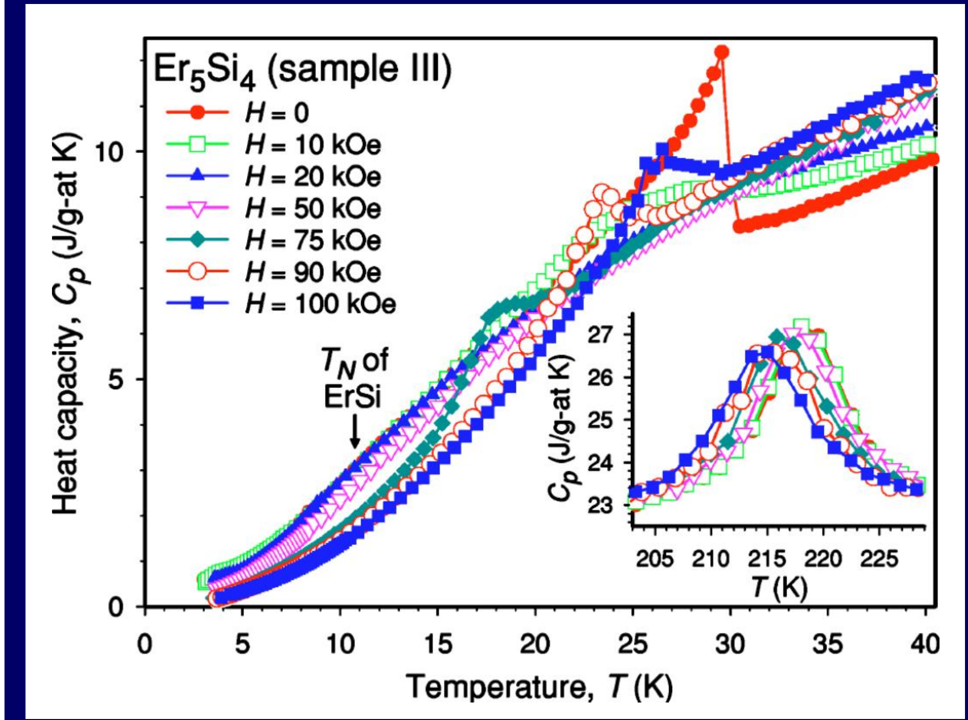
- Structure-dependent magnetism

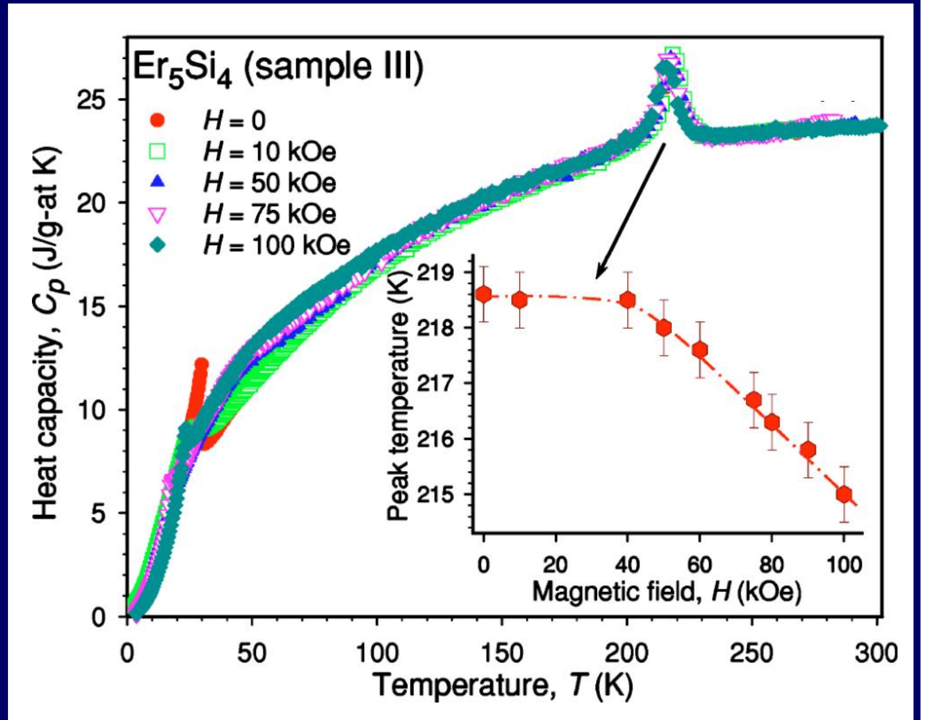
  - *M* is FM ($T_M = 30$ K)
  - *O*(I) is FM ($T_{O(I)} = 36$ K)

Magen et al.
Phys. Rev. B **74**, 134427 (2006).

Er_5Si_4 – Can we do the same with field?

- Heat capacity experiments show some field dependences:
  - At high T, a tiny change of T_t is suggested… REAL?
  - At low T, an anomaly appears and rises upon field.

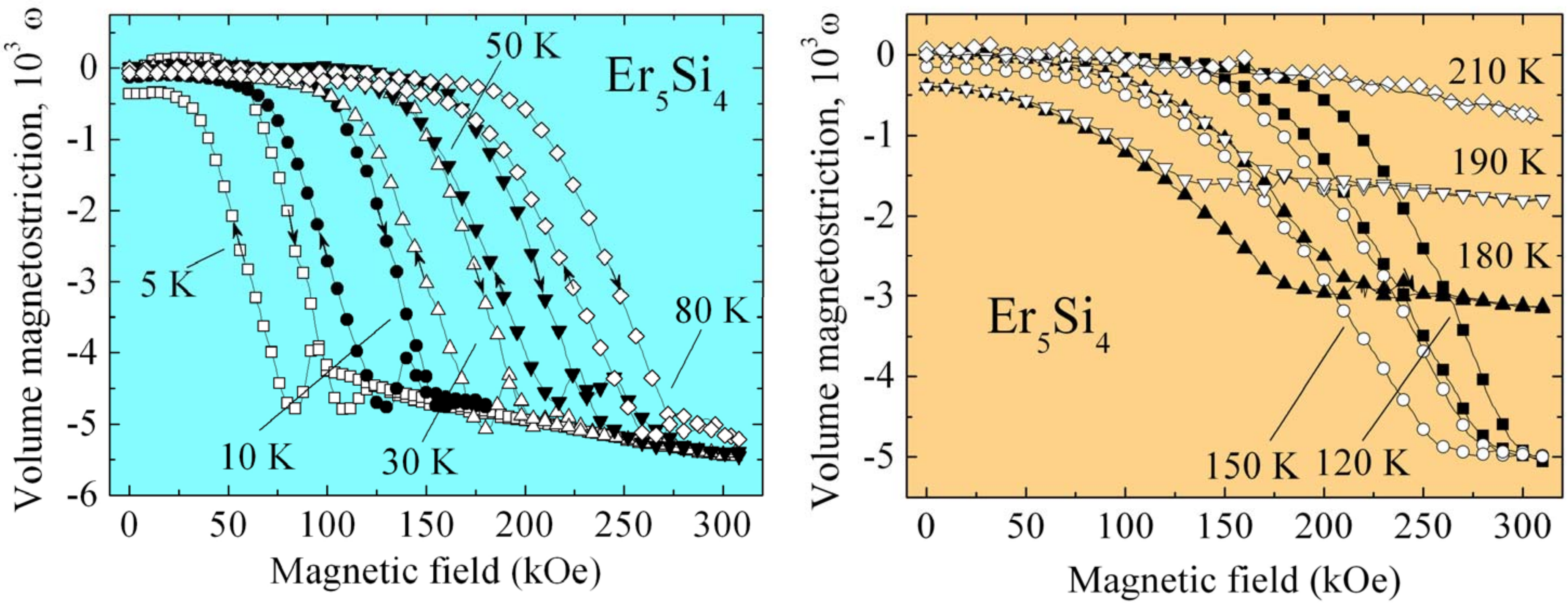




A. O. Pecharsky et al., Phys. Rev. B **70**, 144419 (2004)

Er_5Si_4 – Field induced structural transition

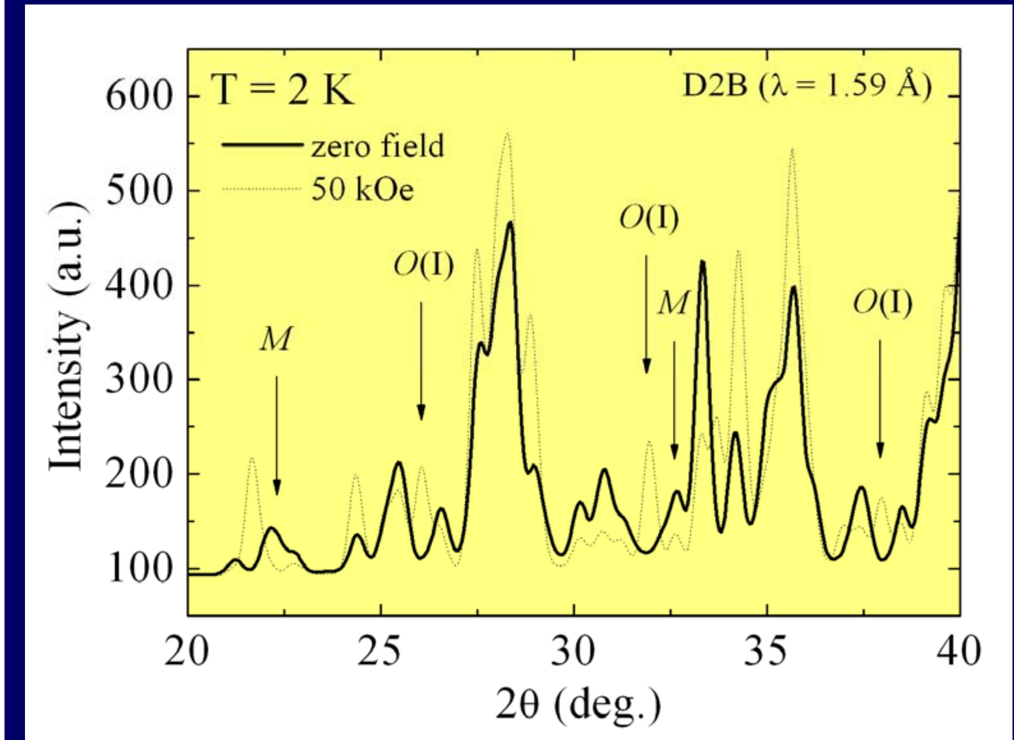
- Field-induced anomaly at low temperature ($M \rightarrow O$(I)?) : $\Delta V/V = -0.5$ %
- It is not evident that magnetic field shifts high temperature $M \rightarrow O$(I)

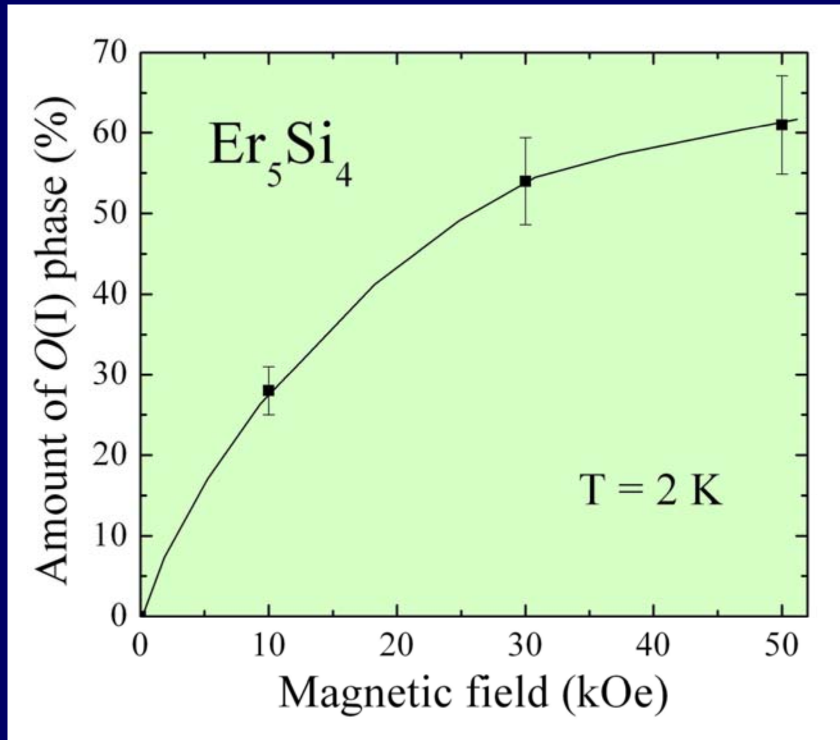


High pulsed magnetic fields (H_{max} = 31 T)

Er_5Si_4 – Field induced structural transition

- Yes! Neutrons show that *O*(I) phase appear at high field (50 kOe).
- …but transformation is again incomplete.

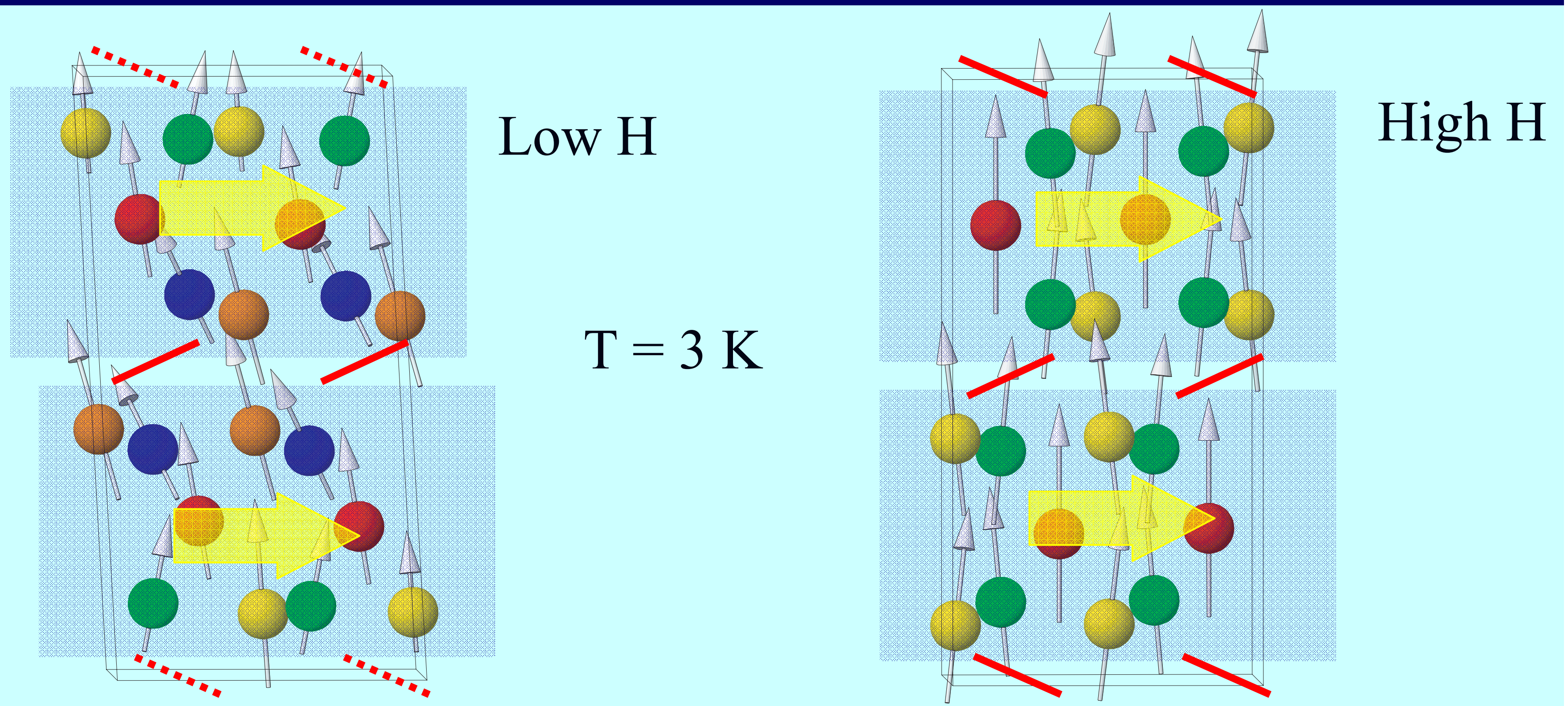




D2B diffractograms vs. H (λ = 1.596 Å)

Er_5Si_4 – Field induced structural transition

- Magnetic field induces the *M*-FM → *O*(I)-FM transformation
- Formation of T'-T' bonds enhances FM → nearly collinear FM structure



D2B diffractograms vs. H (λ = 1.596 Å)

Main Conclusions

► Influence of bonding in the interlayer magnetic coupling.

► Temperature, Magnetic Field and Hydrostatic pressure governs the physical properties of the 5:4 phases:

- Changes de volume cell / crystallographic phase.
- Magnetostructural coupling → change of the magnetic structure.

► Importance of the nature of the magnetic transitions for the magnetocaloric effect:

- 1st order
- Reversible
- Magnetostructurally coupled!

GMCE
Magnetic refrigeration!

Future Work – X-ray vs. H?

- ► $Gd_5(Si_xGe_{1-x})_4$
  - Magnetic structure at low T is unfeasible for neutrons…
  …magnetic diffraction with x-rays at zero-field and $H \neq 0$?
  - Relaxation effect in field induced transition of Gd_5Ge_4.
- ► $Tb_5(Si_xGe_{1-x})_4$
  - Higher fields – is it possible to complete the transition?
  - Support for the SANS scenario/collateral structural effect?
- ► Er_5Si_4
  - Confirmation of complete structural transformation vs H?
  - Is the small shift of the high T transition something real?
- ► $R_5(Si_xGe_{1-x})_4$: unexplored R = Ce, Dy, Tm…
- ► …

Acknowledgements

► MAGNETISM OF SOLIDS GROUP
(ICMA, CSIC-University of Zaragoza, Zaragoza, Spain)

► C. Ritter
(Institute Laue-Langevin, Grenoble, France)

► Z. Arnold & J. Kamarad & O. Prochnenkho & Y. Skorokhod
(Institute of Physics, AS CR, Prague, Czech Republic)

► V. K. Pecharsky & A. O. Tsokol & K. A. Gschneidner, Jr.
(Ames Laboratory, Ames, Iowa, US)

► T. A. Lograsso & D. L. Schlagel
(Ames Laboratory, Ames, Iowa, US)

► J. B. Sousa & J. P. Araujo & A. M. Pereira
(University of Porto, Porto, Portugal)