Phase Transitions in Condensed Matter

Spontaneous Symmetry Breaking and Universality

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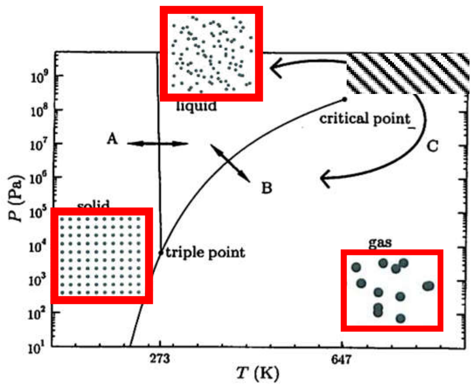
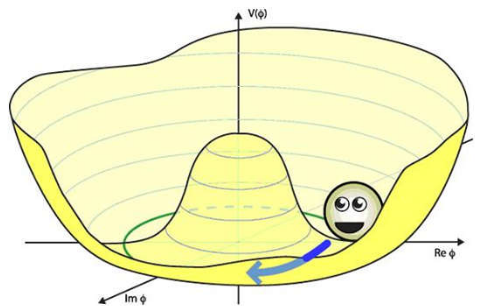
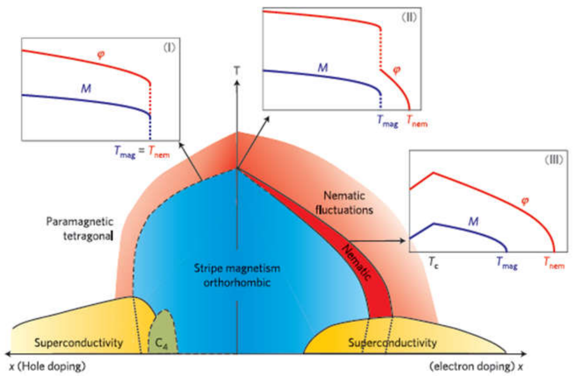






References

[1] **Stephen Blundell, *Magnetism in Condensed Matter***, Oxford University Press

[2] **Igot Herbut, *A Modern Approach to Critical Phenomena,*** Cambridge University Press

[3] **Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena,*** *Oxford Science Pub.*

[4] **Roser Valenti,** *Lecture Notes on* ***Thermodynamics***, *U Frankfurt*

[5] **Matthias Vojta,** *Lecture Notes on* ***Thermal and Quantum Phase Transitions,*** *Les Houches 2015*

[6] **Thomas Palstra,** *Lecture Notes on* ***Multiferroics: Materials and Mechanisms,*** *Zuoz 2013*

Outline

- **Phase transitions in fluids**
  - Phase diagram, order parameter and symmetry breaking
  - Microscopic van-der-Waals theory → universality

- **Magnetic phase transitions in condensed matter**
  - Ferromagnetic phase transition
  - Interacting magnetic dipole moments "spins"
  - Weiss model for ferromagnetism, phase diagram
  - Landau theory

- **Consequences of symmetry breaking**
  - Critical phenomena and universality
  - Excitations, Nambu-Goldstone-, Higgs-modes

- **More complex ordering phenomena**
  - Multiferroics, competing order
  - [Quantum phase transitions]

- **What is a thermodynamic phase?**

  - Equilibrium state of matter of a many body system

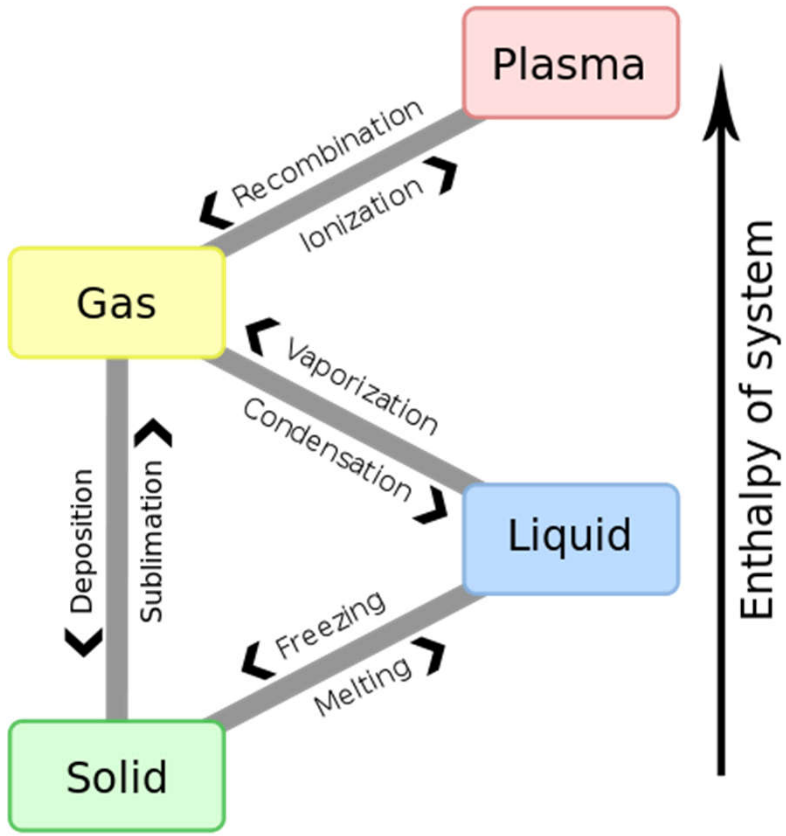
  - **Well defined symmetry**

  - Thermodynamic potential changes analytically for small parameter changes (temperature, pressure, magnetic field)

- **What is a phase transition?**

  - Point in parameter space where the equilibrium properties of a system change *qualitatively*.

  - The system is **unstable w.r.t. small changes** of external parameters



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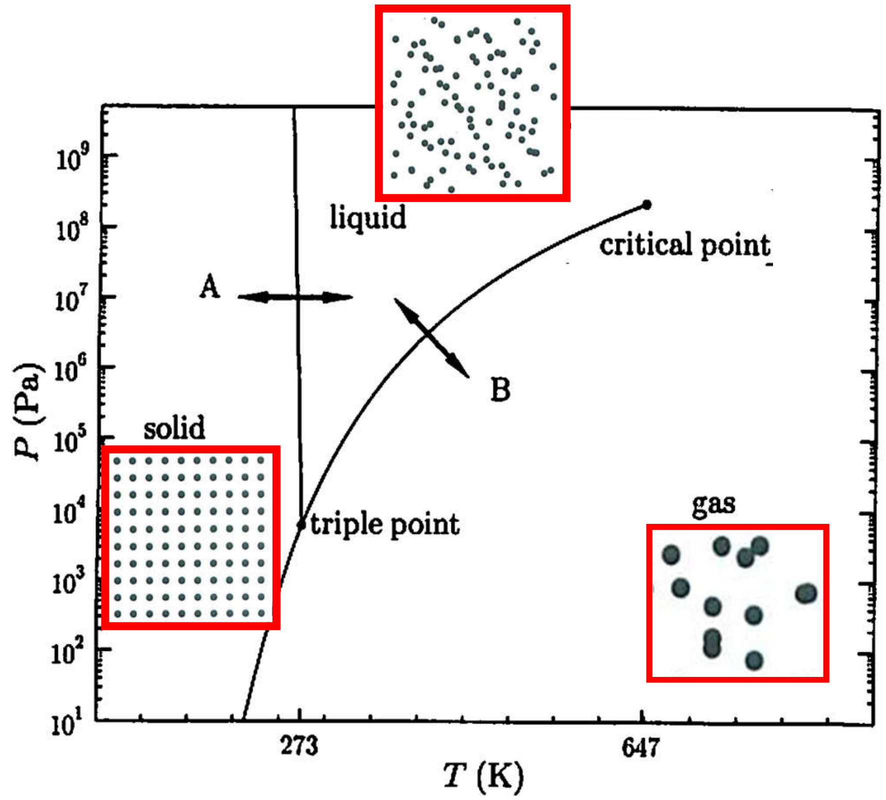
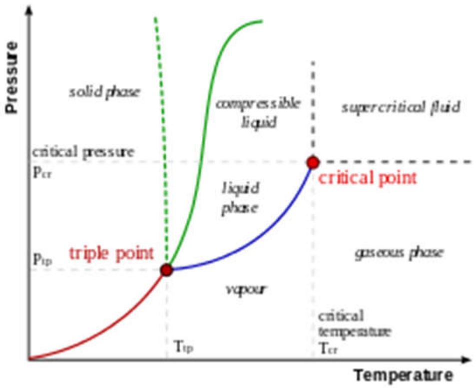
Phase diagram of water

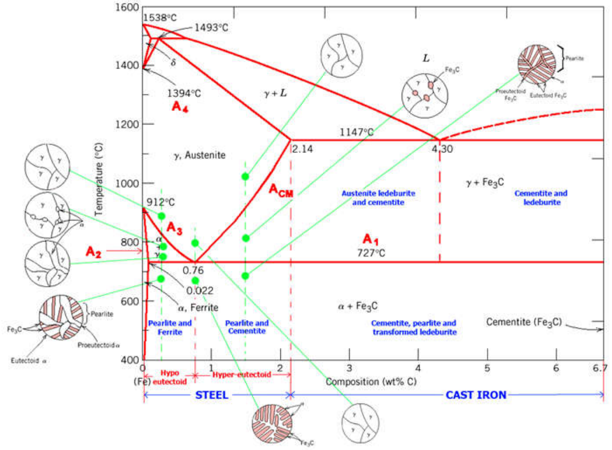


- **Many, many phase diagrams in nature….**

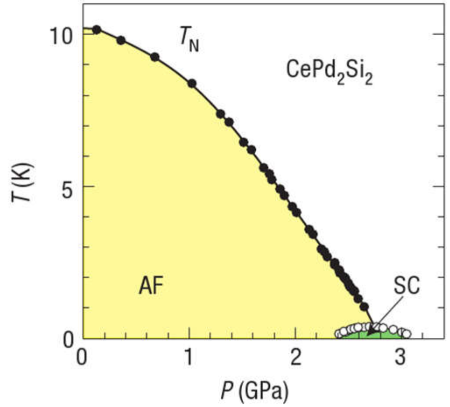
structural phases



wikipedia

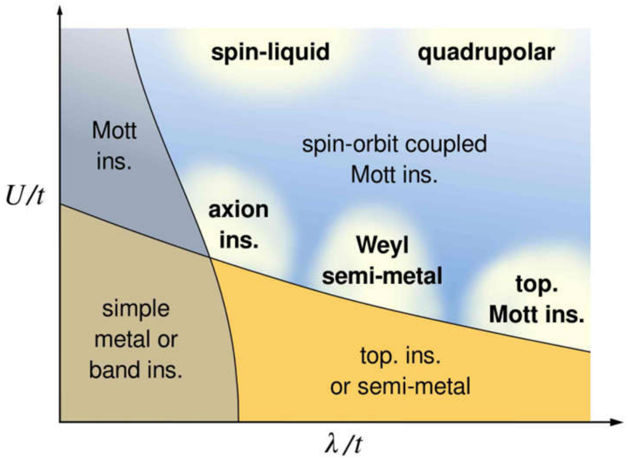


electronic phases

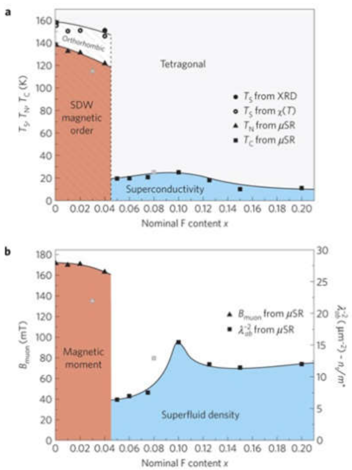


Mathur et al., Nature 1998

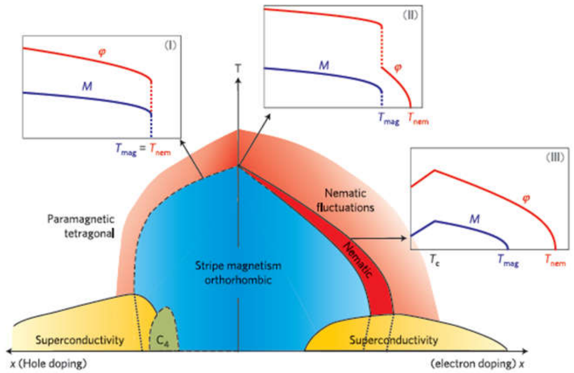
electronic



combined electronic and structural



Luetkens et al., Nature Mat. 2009



Fernandes et al., Nature Phys. 2014

- **What is an order parameter?**

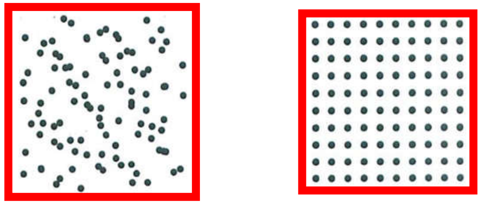
  - observable ϕ which distigiuishes between phases

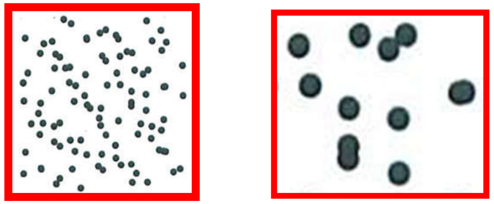
    $< \phi > = 0$ in the disordered phase (high temperature phase)

    $\neq 0$ in the ordered phase

System	Phase transition	Order parameter
H_2O, ^4He, Fe	liquid–solid	fourier component of charge density ρ_G
Xe, Ne, N_2, H_2O	liquid–gas	density difference
Fe, Ni	ferromagnet–paramagnet	magnetization
$RbMnF_2$, La_2CuO_4	antiferromagnet–paramagnet	staggered magnetization
^4He, ^3He	superfluid–normal liquid	superfluid density
Al, Pb, $YBa_2Cu_3O_{6.97}$	superconductor–metal	superfluid density
Li, Rb, H	Bose–Einstein condensation	condensate

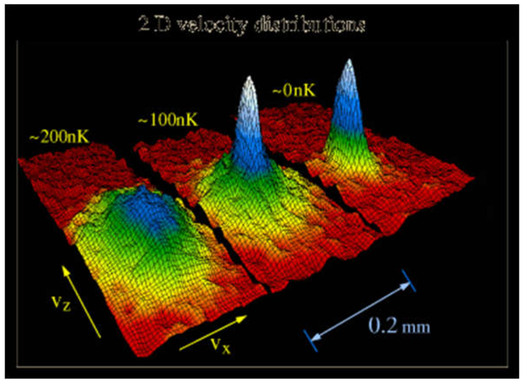
liquid -- solid



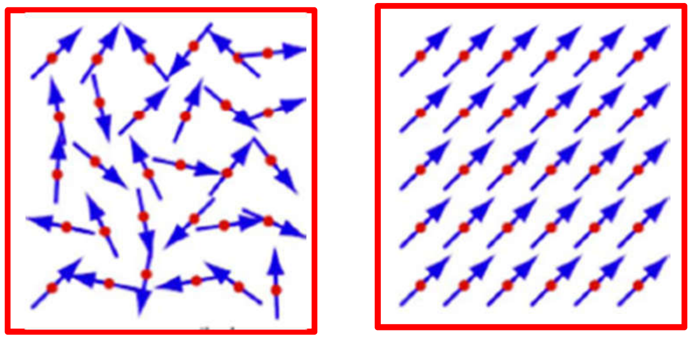


liquid -- gas

Bose-Einstein condensation



paramagnet -- ferromagnet



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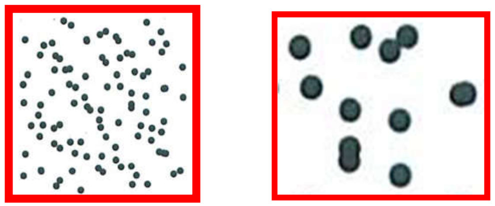
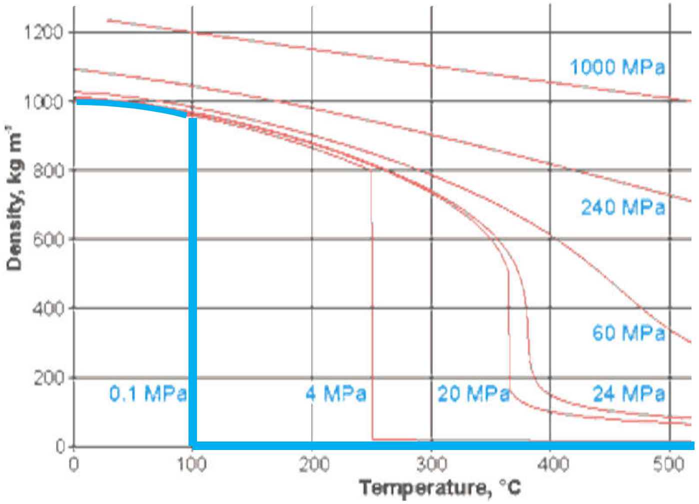
water

liquid gas





- **First order transition**
  order parameter changes discontinuously

  (Ehrenfest definition: first derivative
  of Gibbs free enthalpy G is discontinuous)

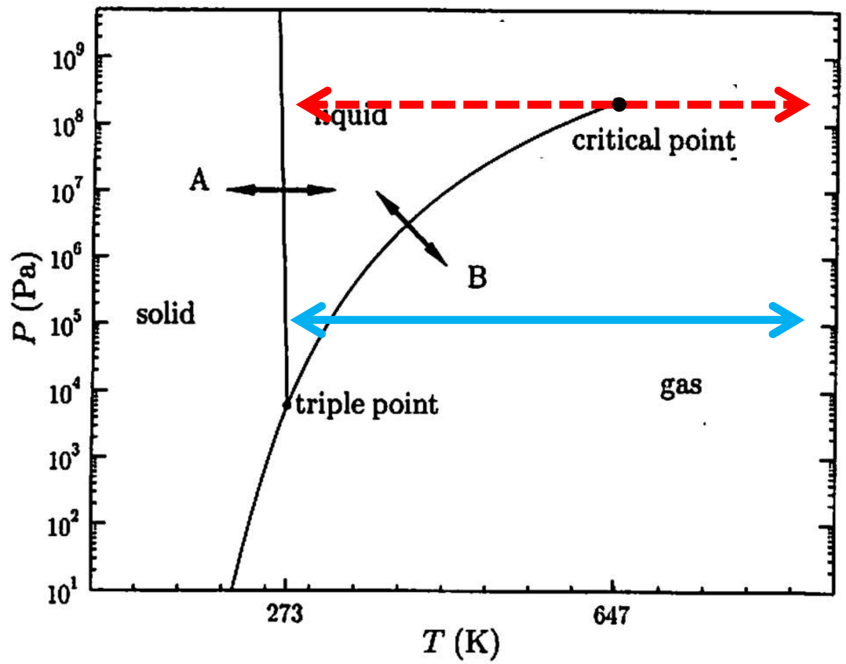
- **Continuous transition**
  order parameter varies continuously

- **Critical point**
  transition point of a continuous transition

  for water @ 647 K and 22.064 MPa

→ liquid to gas phase transition can be of first order or continuous!

Phase diagram of water



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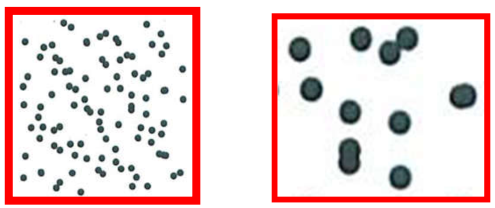
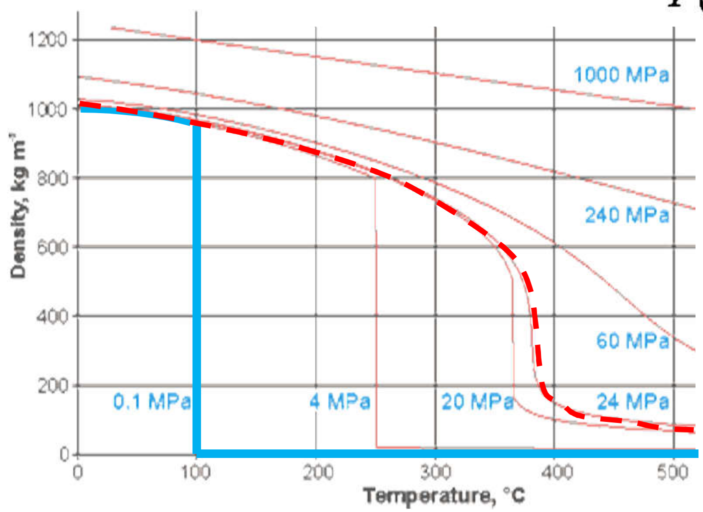
water

liquid -- gas

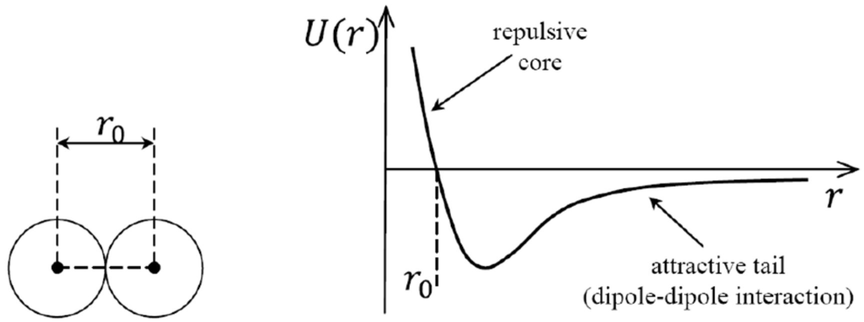




[google]

- **Van- der-Waals-model:**

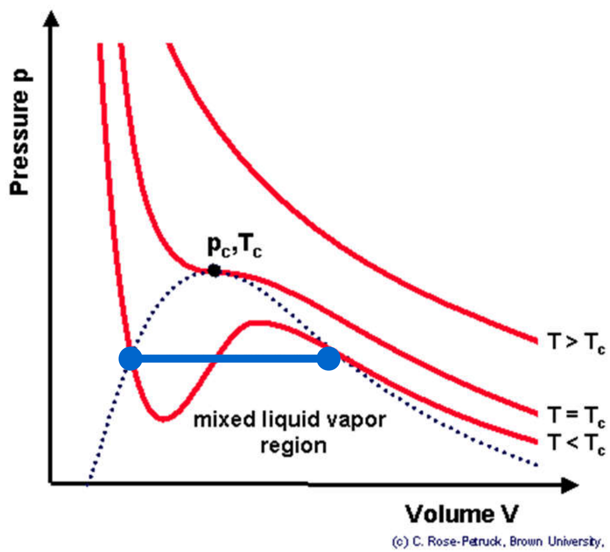
  Attractive particle – particle interaction
  fully rotational invariant V = V(r)
  +
  Finite particle volume



→ van-der-Waals equation

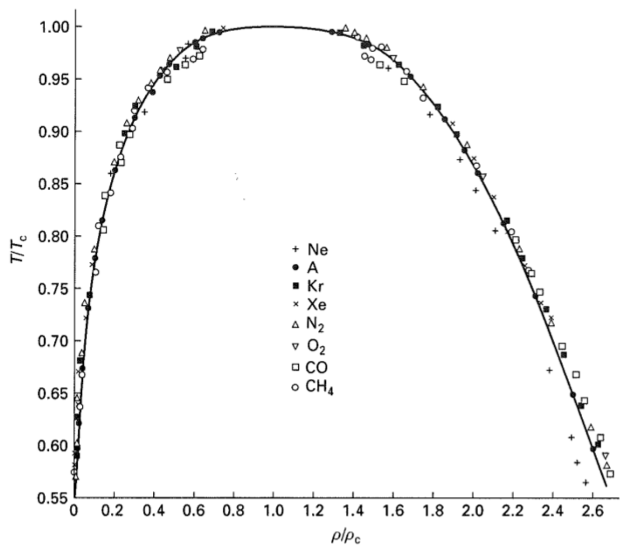
$$(V - bn)\left(P + a\left(\frac{n}{V}\right)^2\right) = nRT$$

- Maxwell construction → isotherms and
  phase coexistence



- **Universal mixed liquid vapor region in p-V diagram for many materials**

  via normalization p/p_c and V/V_c!



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- **Spontaneous symmetry breaking always leads to a phase transition**

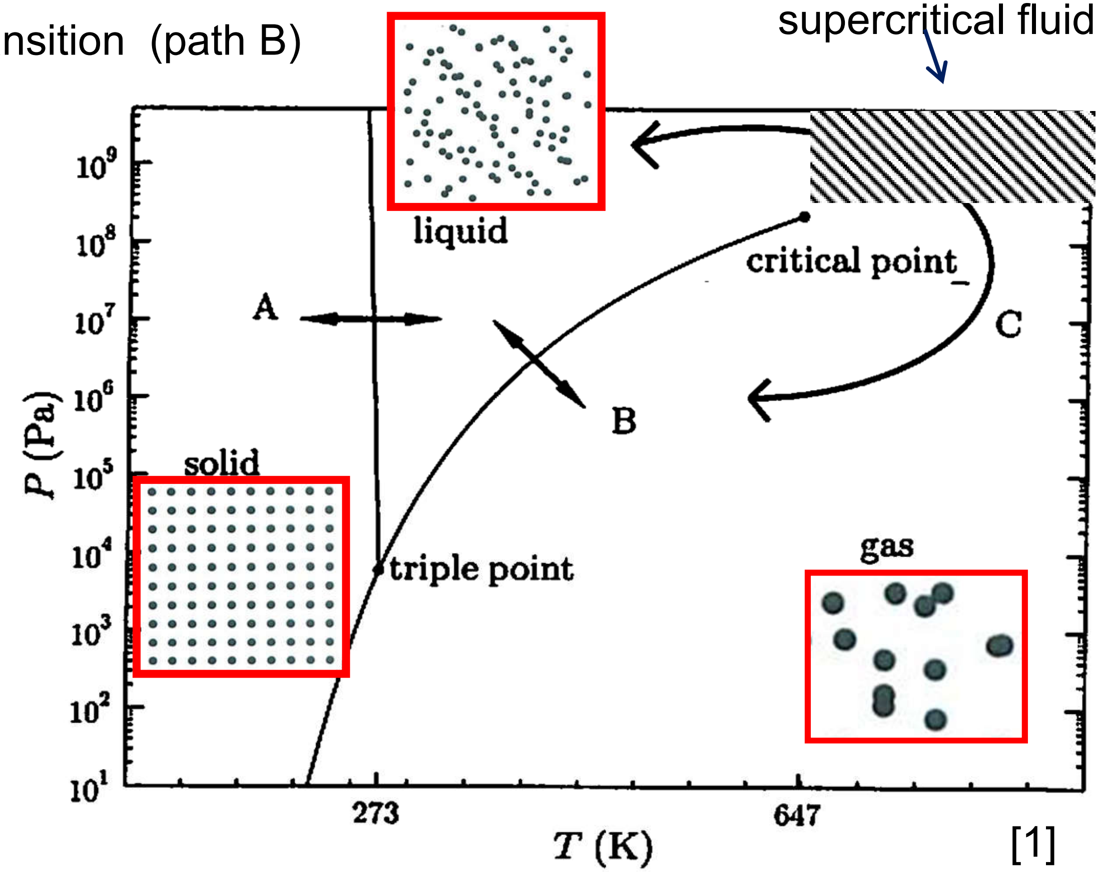
  →no critical end point since symmetry cannot change continuously!
  Example: solid – liquid phase transition (path A)

- **Phase transitions can occur without spontaneous symmetry breaking**

  Example liquid – gas phase transition (path B)

- Continuous crossover from liquid to gas without phase transition via supercritical fluid (path C)

supercritical fluid



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  - Paramagnet
  - Interacting magnetic dipole moments, “spins”
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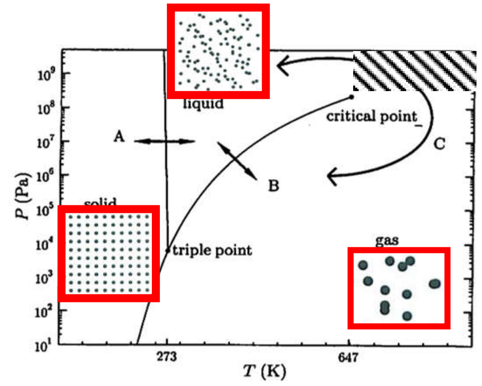
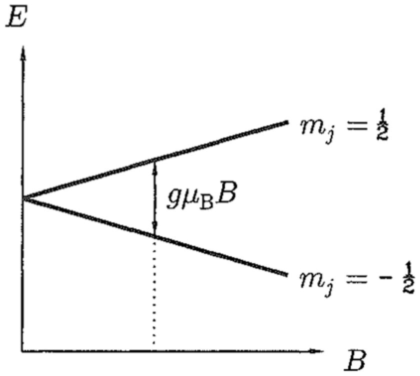
  - [Quantum phase transitions]



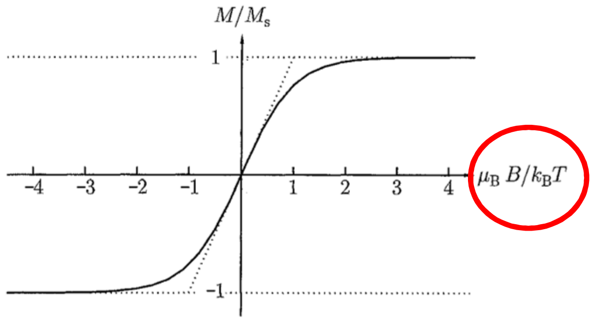
- **Periodic lattice of localized non-interacting magnetic moments**

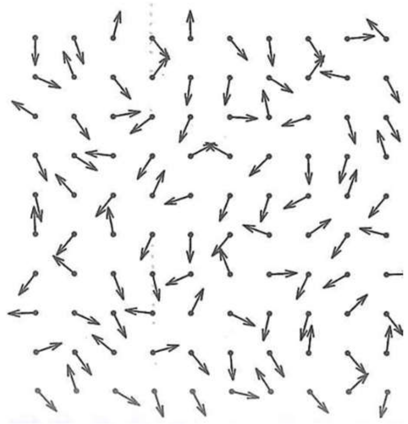
$$\vec{\mu} = g_L \, \mu_B \vec{J}$$

- in external field $\hat{H} = g_L \, \mu_B \, \sum_i \vec{B} \vec{J}_i$



Brillouin function



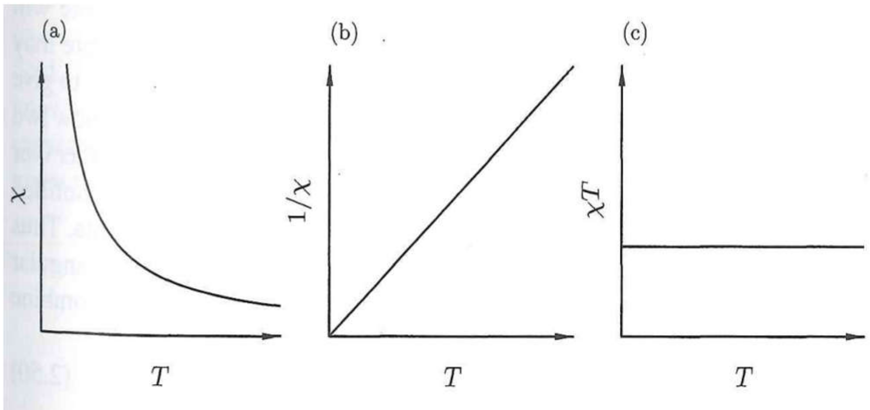


- Magnetic susceptibility :

Curie-law for small B ($g_J \mu_B J B / k_B T$ << 1)

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{n \mu_0 \mu_{\mathrm{eff}}^2}{3 k_B T}$$

$$\mu_{\mathrm{eff}} = g_J \mu_B \sqrt{J(J+1)}$$



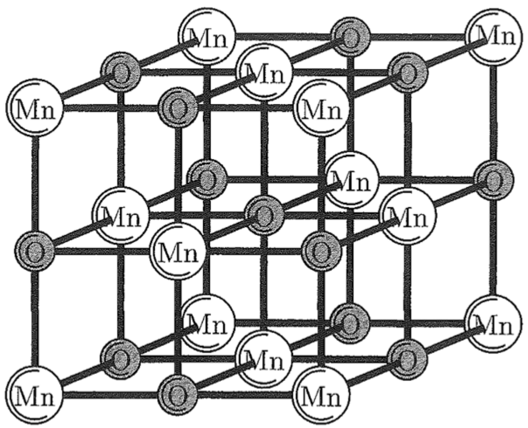
[1]

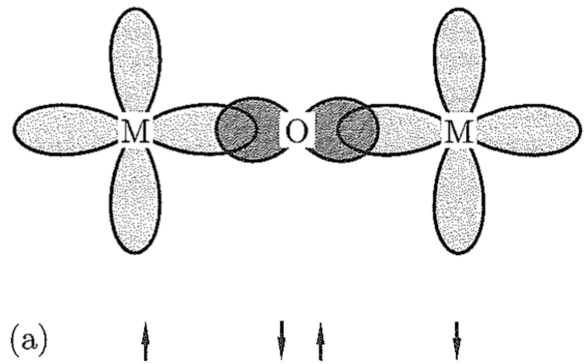
- Interacting magnetic moments:

$$\hat{\mathcal{H}} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_j \mathbf{S}_j \cdot \mathbf{B},$$

- Origin of exchange: spin-dependent Coulomb interaction

e.g. superexchange





[1]

$$\hat{\mathcal{H}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_j \mathbf{S}_j \cdot \mathbf{B},$$

Weiss (1907):

Define an effective magnetic field at site i caused by neighbors j

$$\mathbf{B}_{mf} = -\frac{2}{g\mu_B} \sum_j J_{ij} \mathbf{S}_j$$

„molecular field“

→ single particle problem

$$\hat{\mathcal{H}} = g\mu_B \sum_i \mathbf{S}_i \cdot (\mathbf{B} + \mathbf{B}_{mf})$$

Ansatz: B_{mf} ~ Magnetization M

$$\mathbf{B}_{\mathrm{mf}} = \lambda \mathbf{M}$$ with $$\lambda = \frac{2zJ}{ng^2\mu_B^2},$$

→ Two linear independent equations

$$\frac{M}{M_s} = B_J(y)$$

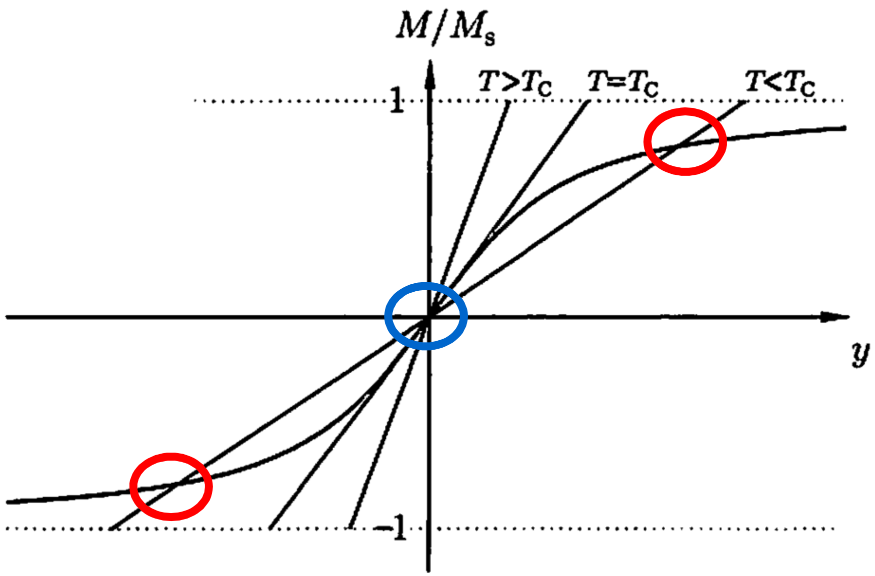
$$y = \frac{g_J \mu_B J (B + \lambda M)}{k_B T}$$

B_J = Brillouin function

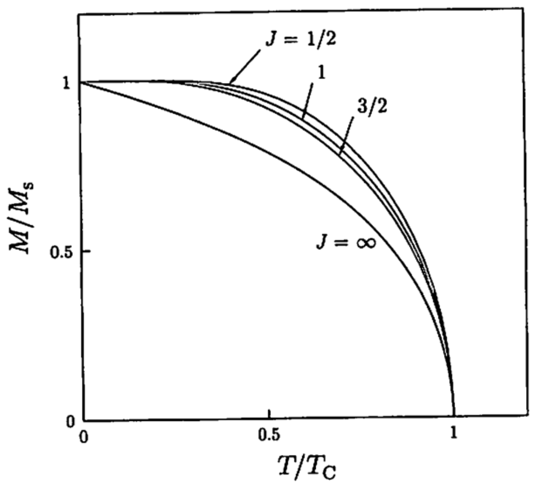
Magnetization of a paramagnet

in total magnetic field $B + \lambda M$

Graphical Solution



Continuous phase transition



[1]

M=0 always possible

$M \neq 0$ only if $T < T_C$

$$T_C = \frac{2zJJ(J+1)}{3k_B}$$

T_C ~ exchange energy J,
number of neighbors
size of moments

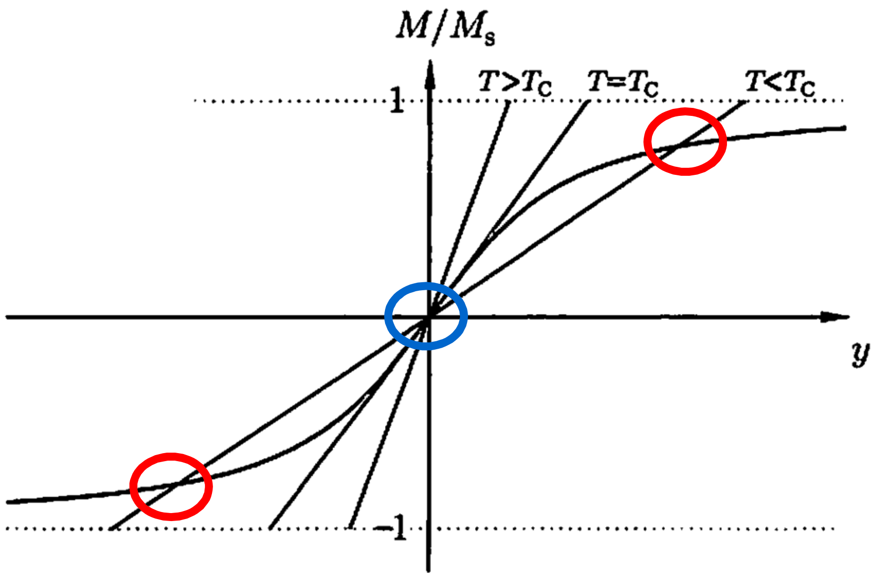
Typical:

$J = \frac{1}{2}$ and $T_C \sim 10^3$ K

$B_{mf} = k_B T_C / \mu_B \sim 1500$ T.

Huge!

Graphical Solution



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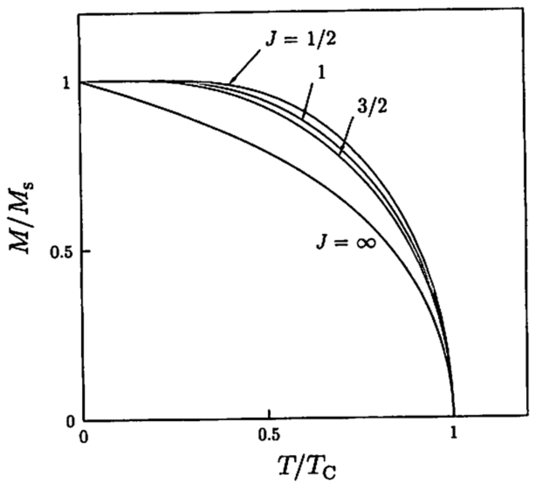

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$M \neq 0$ only if $T < T_C$

$$T_C = \frac{2zJ\,J(J+1)}{3k_B}$$

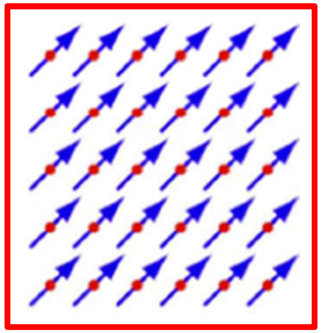
T_C ~ exchange energy J,
number of neighbors
size of moments

- Universal T dependence of order parameter
- depends only on total angular momentum multiplicity J

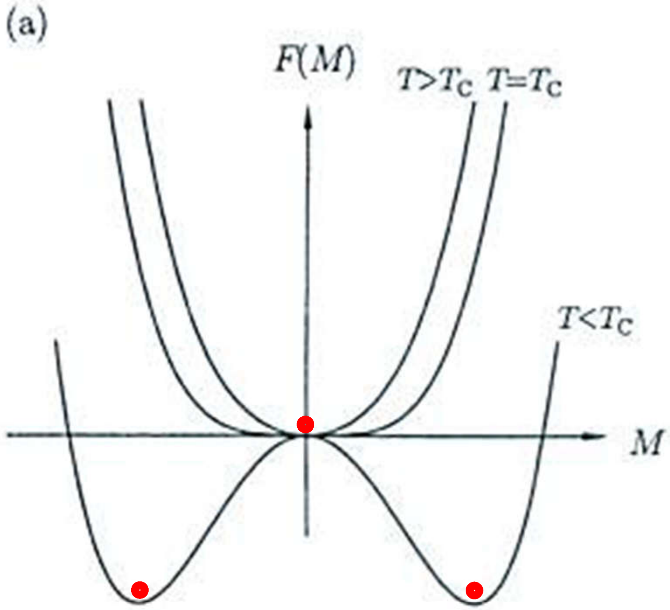
- Hamiltonian has full rotational symmetry in space (scalar product is invariant)

$$\hat{\mathcal{H}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

- Ferromagnetic state has a reduced symmetry (invariant only under rotation around M)



$$\boldsymbol{M} = \frac{\sum \mu_i}{V}$$

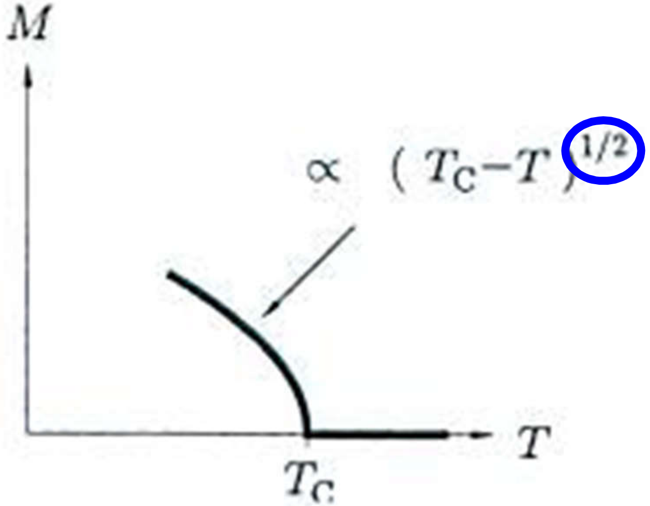


$$F(M) = F_0 + a(T)M^2 + bM^4$$

$$a(T) = a_0(T - T_C)$$

$$\partial F/\partial M = 0$$

$$M = 0 \text{ or } M = \pm\left[\frac{a_0(T_C - T)}{2b}\right]^{1/2}$$



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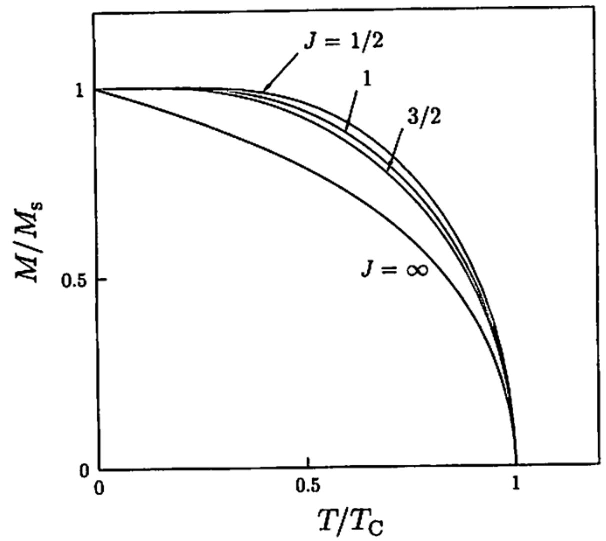
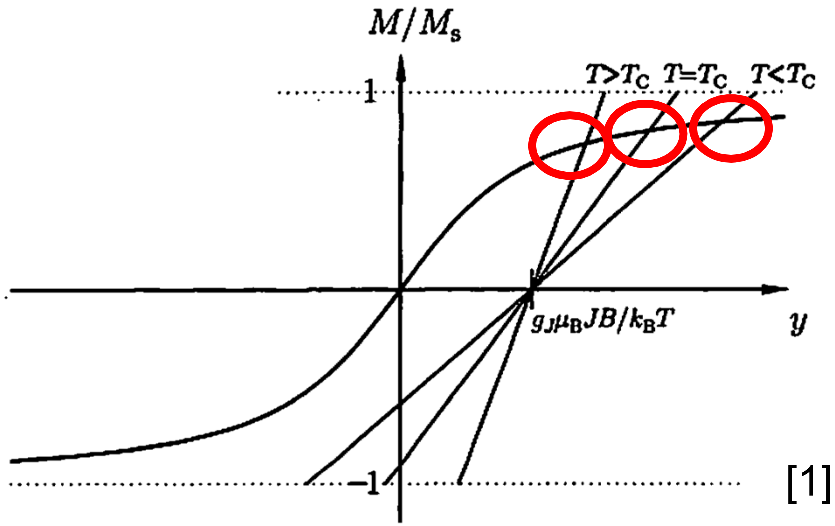
crf Weiss theory:



In magnetic field: Magnetization parallel to field is always > 0
→ No phase transition !



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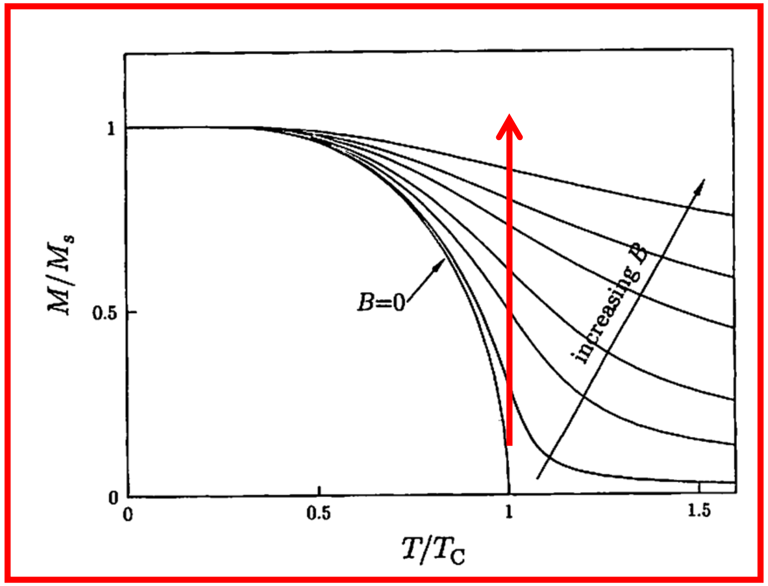
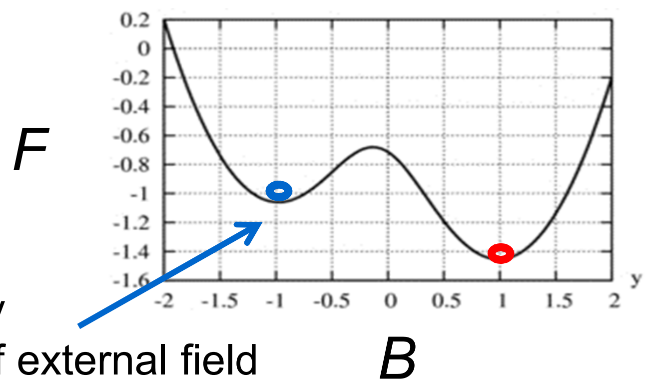


[1]

Explicit symmetry breaking due to Zeeman term

$$\hat{\mathcal{H}} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_j \mathbf{S}_j \cdot \mathbf{B},$$

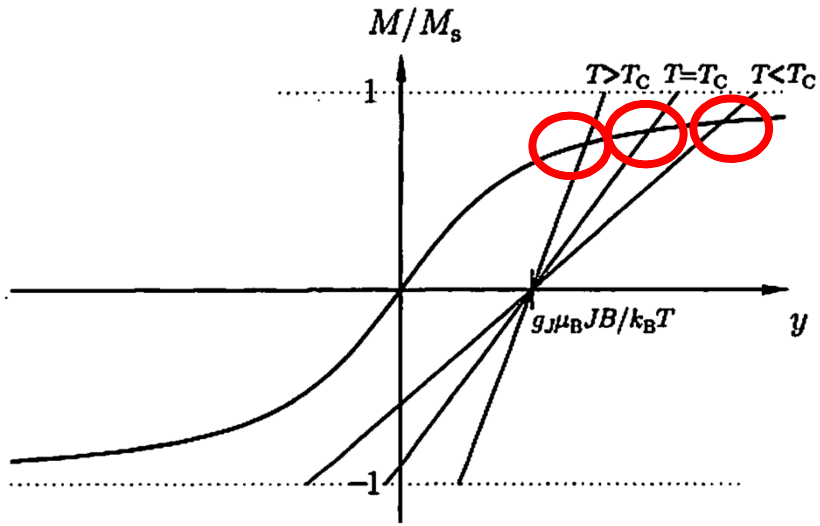
$$F(M) = F_0 + a(T)M^2 + bM^4 \quad \boldsymbol{M}\mathbf{B}$$

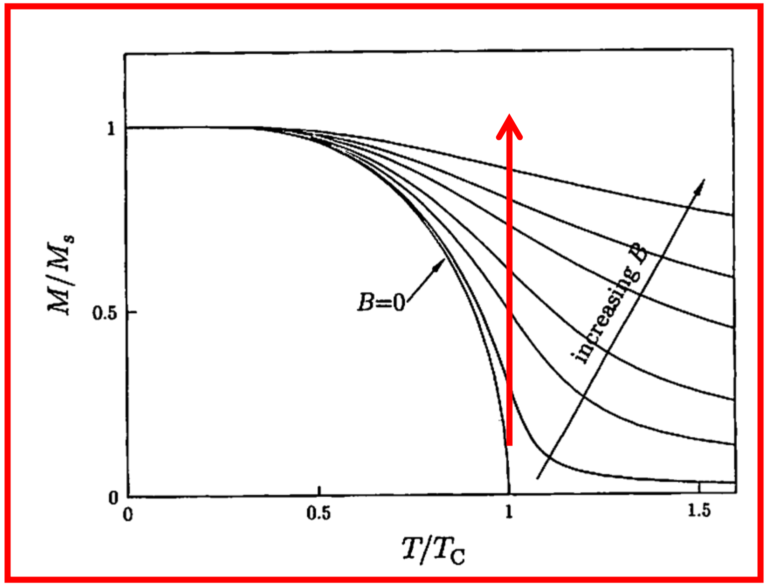


M < 0 metastable solution exists for small B only
→ First order transition below T_C as a function of external field

[Web]

Solution in magnetic field: Magnetization parallel to field always > 0
→ No phase transition !





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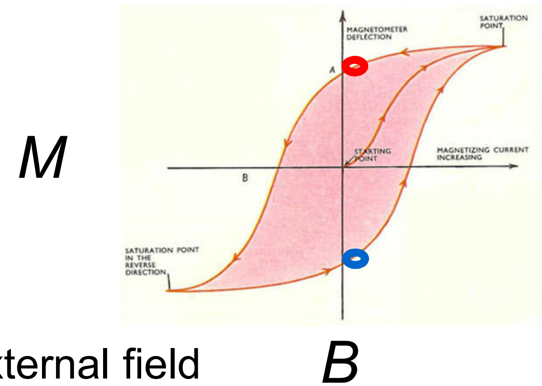

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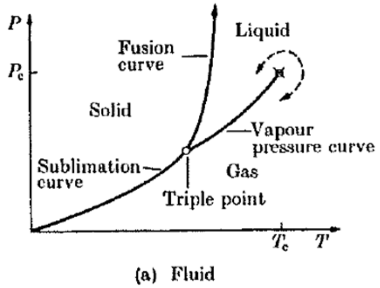
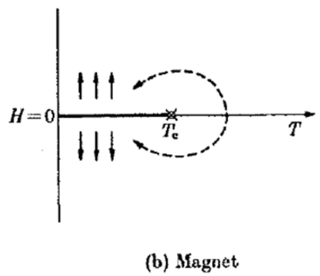
[Web]

Comparison of fluid and magnet phase diagrams

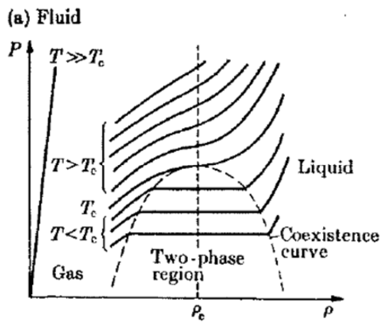
pressure-temperature



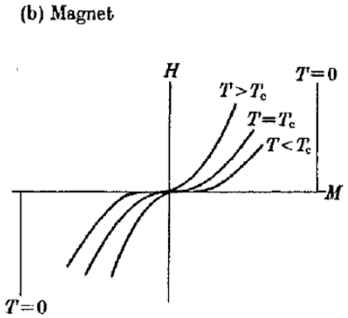
magnetic field-temperature plane



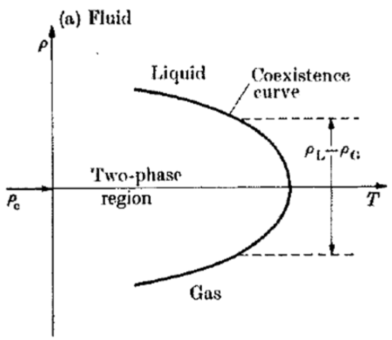
pressure-density plane



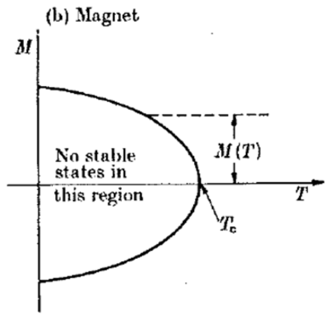
magnetic field-magnetisation plane



density-temperature



magnetisation-temperature plane



$$dU = TdS + \sum_{i=1}^{m} F_i dq_i$$

for fluid $\{F, q\} \rightarrow \{-P, V\}$

Sometimes density ρ = N m / V used

Gibbs free energy

G = U –TS + p V

for magnet $\{F, q\} \rightarrow \{\mathcal{B}, \mathcal{M}\}$

Gibbs free energy

G = U –TS – *M* B

[3,5]

Outline

- **Phase transitions in fluids**
  - Phase diagram, order parameter and symmetry breaking
  - Microscopic van-der-Waals theory → universality

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  - Interacting magnetic dipole moments, “spins”
  - Weiss model for ferromagnetism → universality
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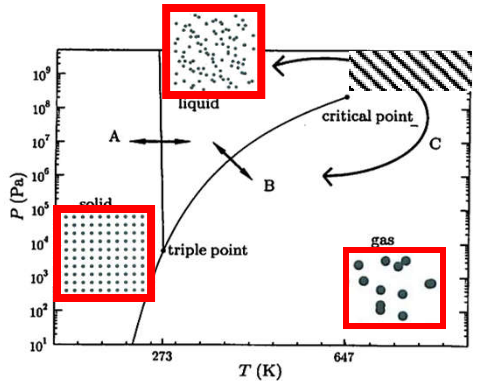
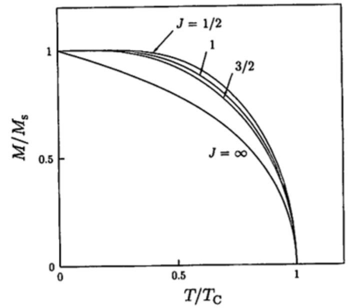
- **Consequences of symmetry breaking**
  - Critical phenomena and universality
  - Excitations, Nambu-Goldstone-, Higgs-modes

- **More complex ordering phenomena**
  - Multiferroics, competing order
  - [Quantum phase transitions]





Critical phenomena and universality

Result of renormalisation group theory (Wilson) and of numerical calculations:

For continuous phase transitions the behavior close to the critical point (T_c) (i.e. the critical exponents $\alpha,\beta,\gamma,\delta$) depends only on a few parameters:

- Dimensionality of the order parameter Ordnungsparameters d
- Dimensionality of the interaction D
- Is the interaction long-range (power law decay r^{-n}, i.e. no length scale) or short range (exponential decay exp $(-r/r_0)$, i.e. length scale r_0) ?

Response functions

heat capacity $C_V \sim |T - T_c|^{-\alpha}$

isothermal compressibility $\kappa_T \sim (T - T_c)^{-\gamma}$

magnetic susceptibility

$$\chi \propto (T - T_C)^{-\gamma}$$

Order parameter

$$\Delta\rho \sim (T - T_c)^{\beta}$$

$$\frac{p}{kT_c} \sim \text{const.} + \text{const.}(\rho - \rho_c)^{\delta}$$

$$M \propto (T_C - T)^{\beta}$$

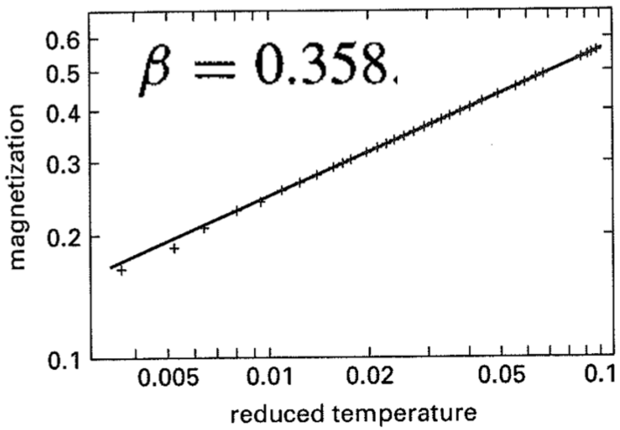
$$M \propto H^{1/\delta}$$

Critical phenomena and universality

Widom scaling relation $\delta = 1 + \gamma/\beta$

exponent	value vdW (mean field)	experimental value	Ising	Ising	Heisenberg
α	0	0.1			
β	0.5	0.33	$\frac{1}{8}$	0.326	0.367
γ	1	1.35	$\frac{7}{4}$	1.2378(6)	1.388(3)
δ	3	4.2	15	4.78	4.78
dimensionality of the interaction D			1	1	3
dimensionality of the order parameter d			2	3	3

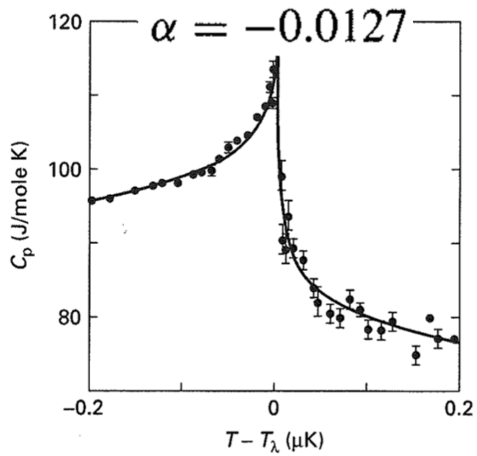
$M \propto (T_C - T)^\beta$



Magnetization vs. reduced temperature in nickel

[2]

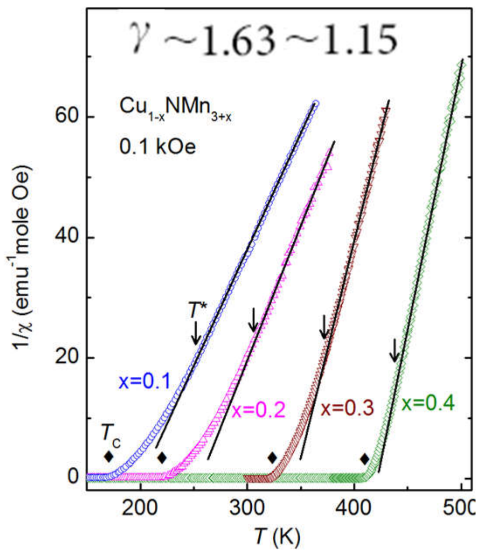
$C_P = B + A_{\pm}|t|^{-\alpha}/\alpha$



Specific heat at constant pressure near the superfluid transition in ^{4}He.

[2]

$1/\chi_0 \sim (T/T_C - 1)^\gamma$



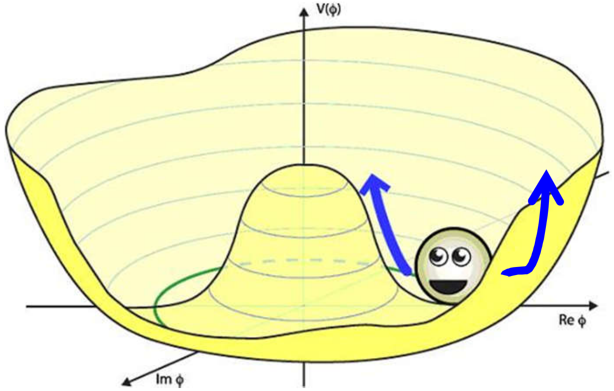
[2]

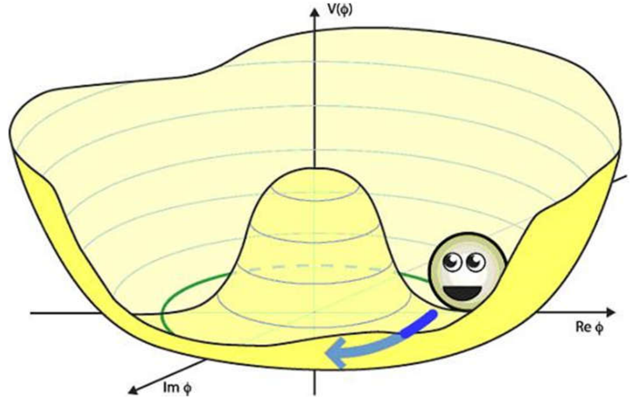
Excitations in the symmetry broken state of a continuous symmetry

Excitations = time dependent fluctuations of the order parameter

- massive excitation

massless Nambu-Goldstone-Bosons





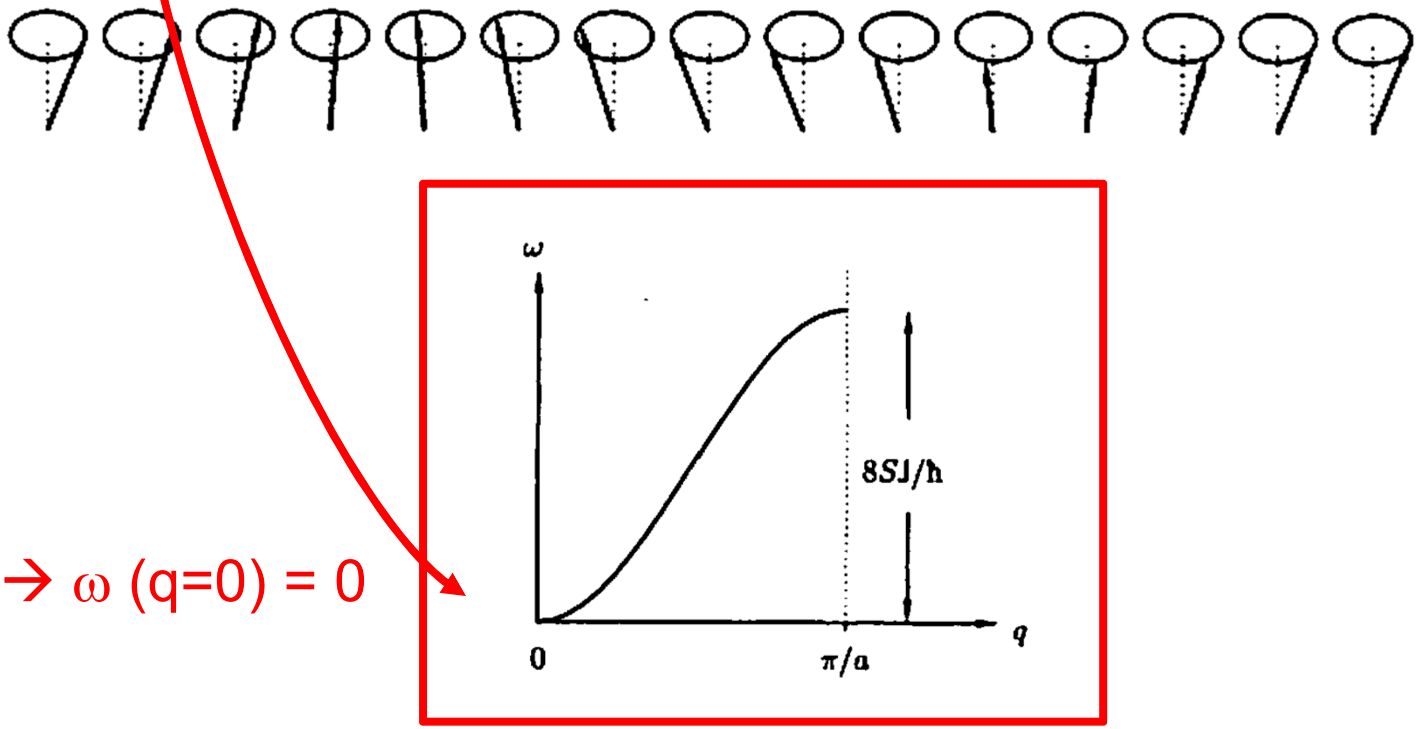
Variation of the absolute value of the order parameter
„amplitude mode“
„Higgs mode“

Continuous rotation of the order parameter connecting different equivalent ground states with the same absolute value
„phase mode“

Nambu-Goldstone excitation: k=0 magnon in the Heisenberg model

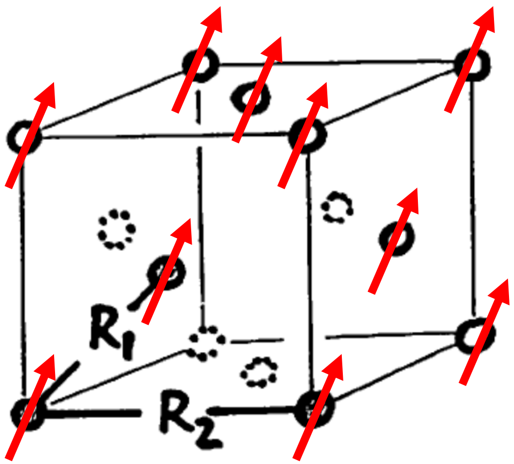
Short range interactions: $\hat{\mathcal{H}} = -\sum_{\langle ij \rangle} J \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$

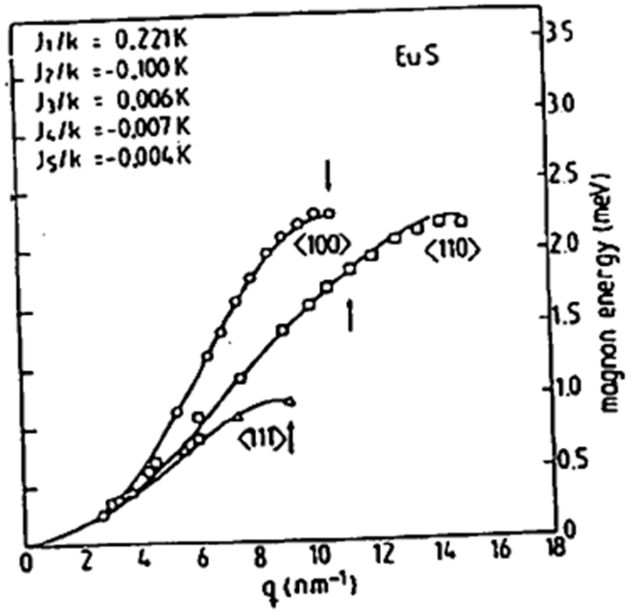
1-D chain $\hat{\mathcal{H}} = -2J \sum_i \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1}$.



→ ω (q=0) = 0

EuS: Ferromagnet (T_C = 16,5 K) with localized magnetic moments





face centered cubic

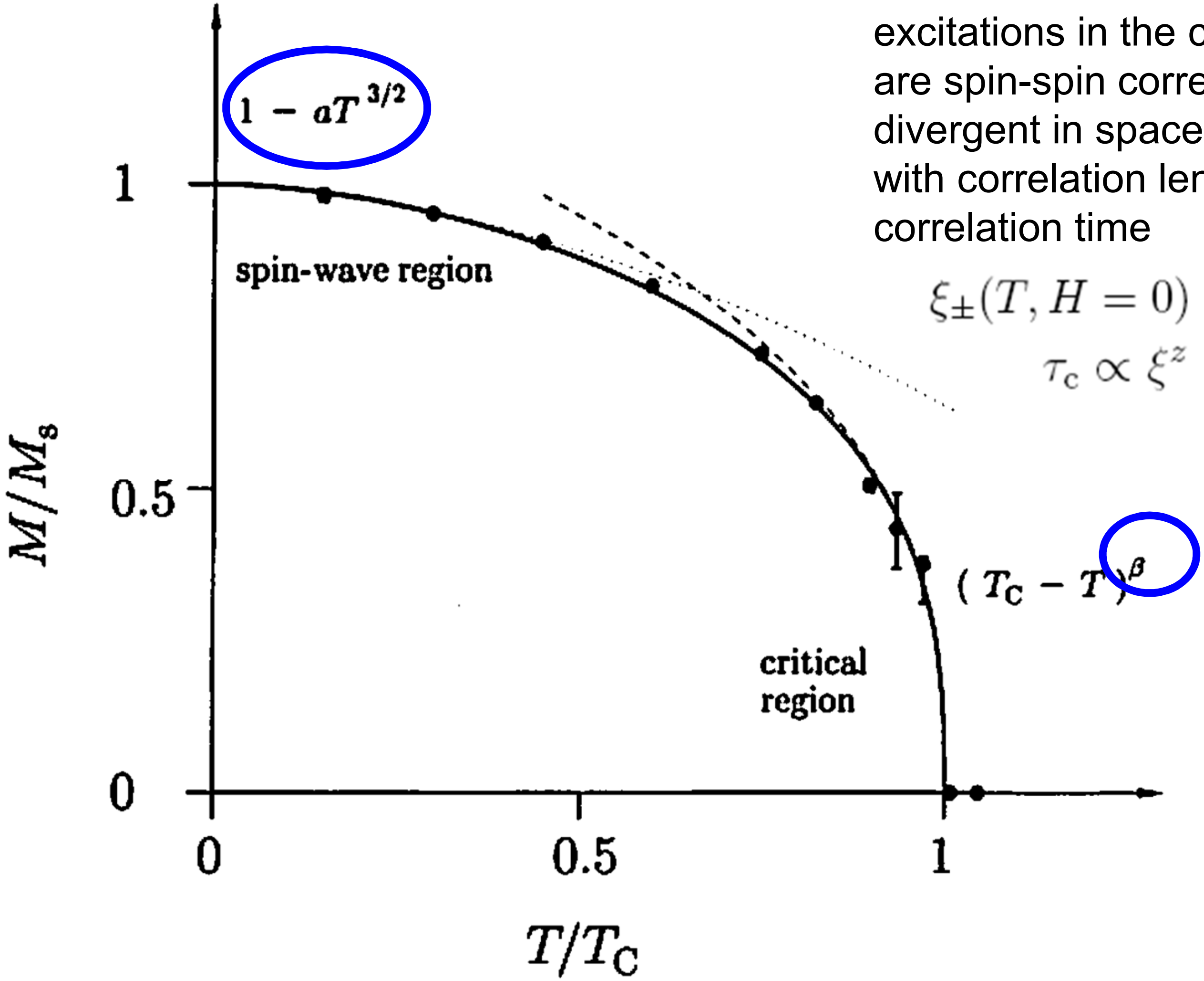
Eu^{2+} ($4f^7$): J=S=7/2 ions

Isotropic Heisenberg interaction of nearest neighbor spins:

$$H = -\sum_{n,m} J_{nm} S_n S_m$$

Magnons are
low temperature excitations

$$\hat{\mathcal{H}} = -\sum_{\langle ij \rangle} J\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$



excitations in the critical region are spin-spin correlations divergent in space and time, with correlation length and correlation time

$$\xi_{\pm}(T, H=0) \propto |t|^{-\nu}$$

$$\tau_c \propto \xi^z \propto |t|^{-\nu z}$$

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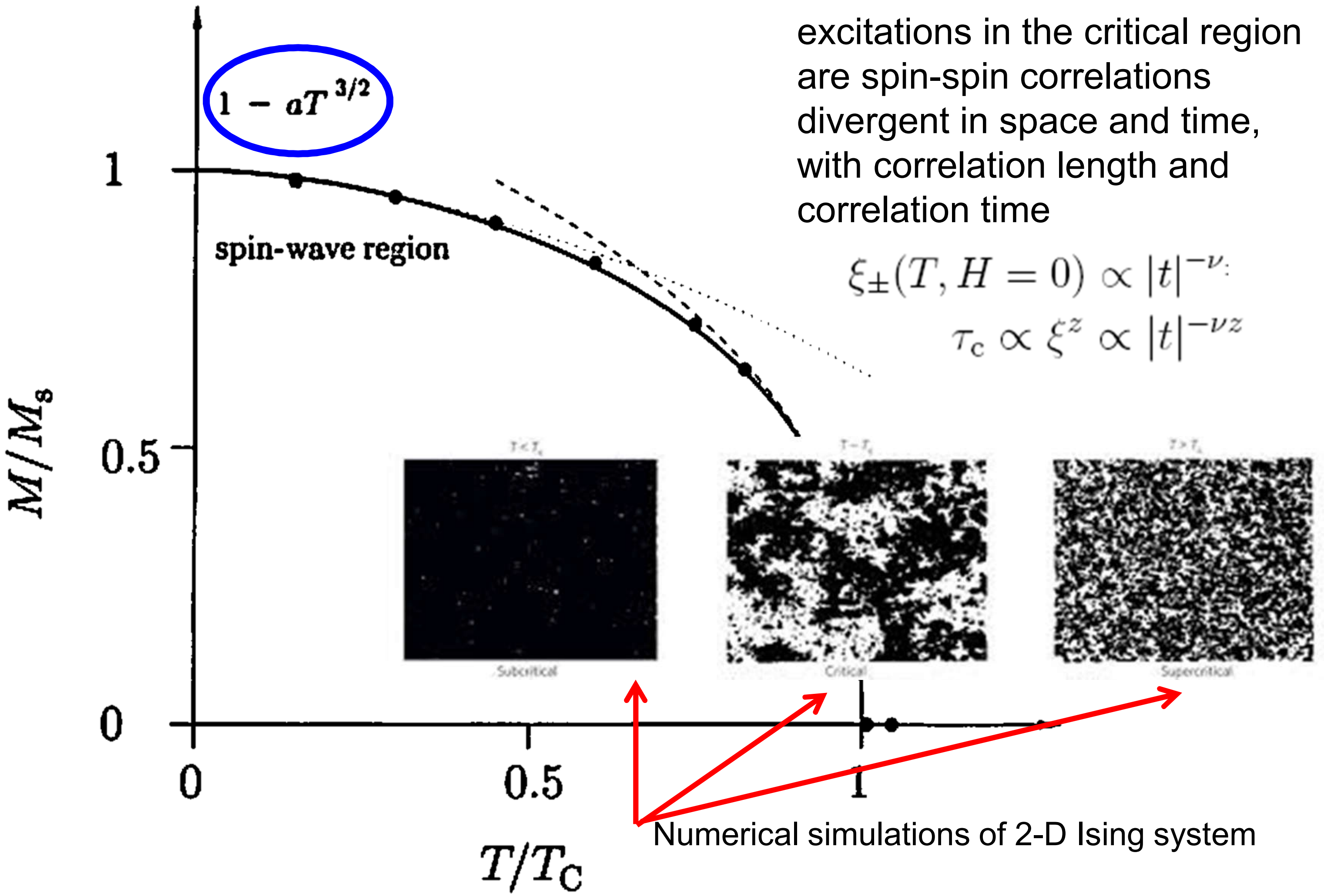

Numerical simulations of 2-D Ising system

Ginzburg-Landau

Energy increase through spatial fluctuations of the order parameter

For a Ferromagnet one direction of M is spontaneously choosen
→ Spatial fluctuations are e.g. rotations of the local order parameter

→ Energy increase $\Delta E \sim (\nabla M)^2$

This holds in general for order parameters and is described by the Ginzburg-Landau-Theory (crf. Superconductivity, Brout-Engert-Higgs):
For charged particles (here Cooper pairs with charge 2e)
this leads to the canonical momentum term (principle of minimal coupling)

$$f = \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}\left|(-i\hbar\nabla + 2eA)\psi\right|^2 + \frac{1}{2\mu_o}(B - B_E)^2$$

Overview spontaneous symmetry breaking

Phenomenon	High T Phase	Low T Phase	Order parameter	Excitations	Rigidity phenomenon	Defects
crystal	liquid	solid	ρ_G	phonons	rigidity	dislocations, grain boundaries
ferromagnet	paramagnet	ferromagnet	$\mathbf{M}$	magnons	permanent magnetism	domain walls
antiferromagnet	paramagnet	antiferromagnet	$\mathbf{M}$ (on sublattice)	magnons	(rather subtle)	domain walls
nematic (liquid crystal)	liquid	oriented liquid	$S = \langle \frac{1}{2}(3\cos^2\theta - 1) \rangle$	director fluctuations	various	disclinations, point defects
ferroelectric	non-polar crystal	polar crystal	$\mathbf{P}$	soft modes	ferroelectric hysteresis	domain walls
superconductor	normal metal	superconductor	$\lvert\psi\rvert e^{i\phi}$	–	superconductivity	flux lines

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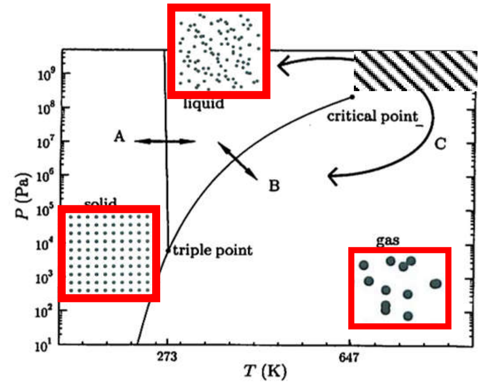
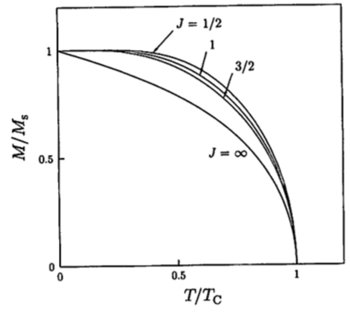
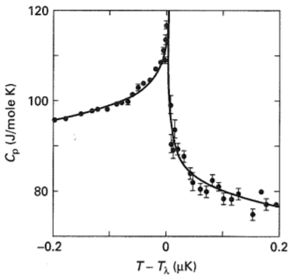






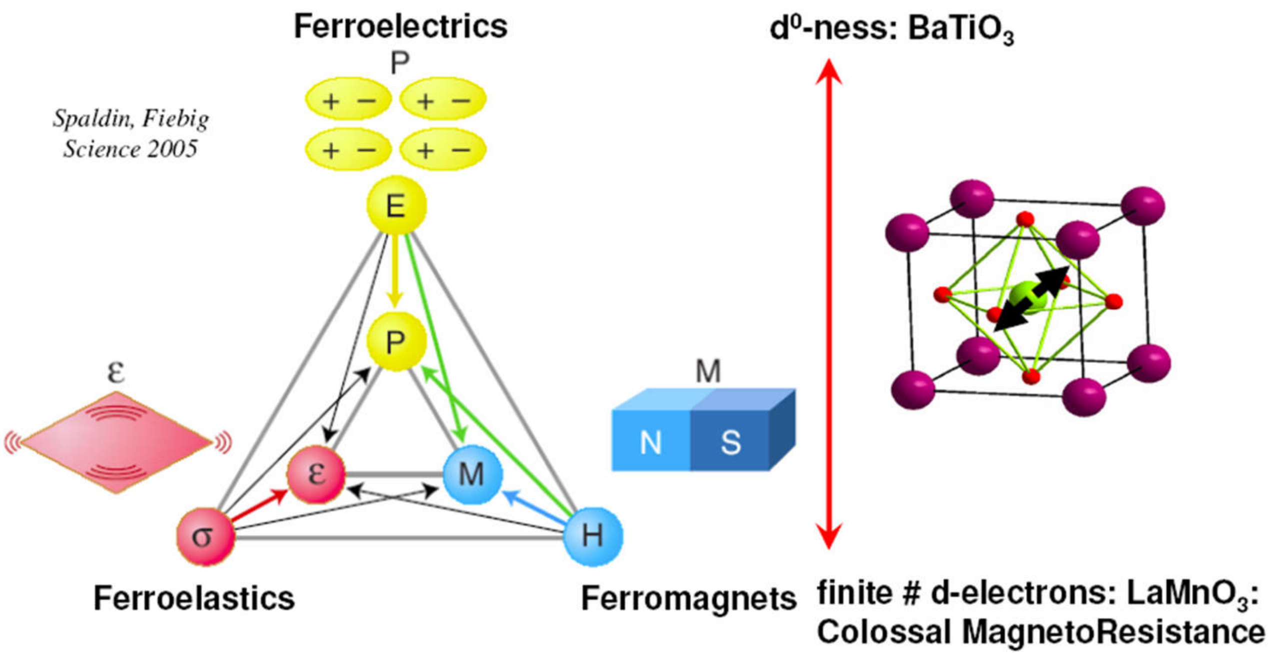
Multiferroics

Ferromagnet: spontaneous M: magnetization — **time reversal**

Ferroelastic: spontaneous ε : strain — **displacements**

Ferro-electric: spontaneous P: polarization — **inversion symmetry**

Design of Materials with Strong Magneto-Electric Coupling



Exceptions:magnetoelectrics: Cr_2O_3
multiferroics: $BiMnO_3$

Multiferroics

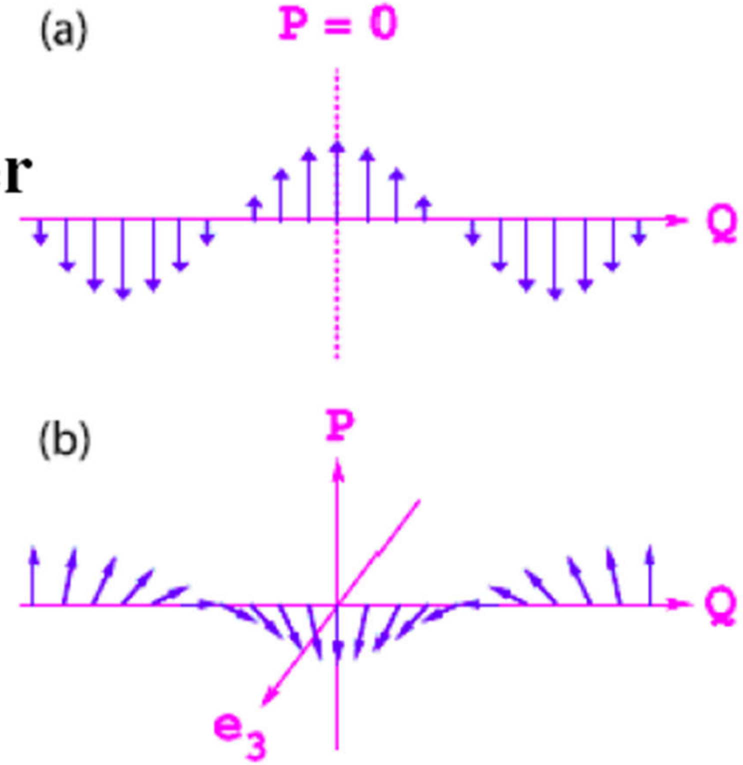
Magnetically induced ferroelectricity

Sinusoidal magnetic order

P=0

Helical magnetic order

$$\mathbf{P} = \gamma\chi e M_1 M_2 \, [e_3 \times Q]$$



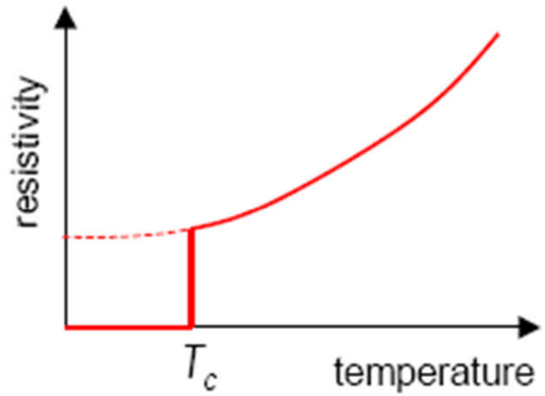
exchange striction
magnetic frustration
secondary order parameter

Figure 1: The sinusoidal spin density wave might give rise to local polarizations but the average polarization is always zero (a). For the helical spin density wave the average polarization is nonzero and perpendicular to the spin rotation axis and the wave vector (b) .

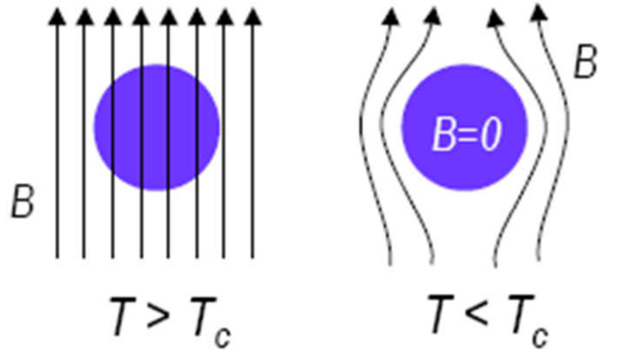
*M Mostovoy, PRL **96**. 067601 (2006), Nagaosa PRL 2006*

Conventional Superconductivity

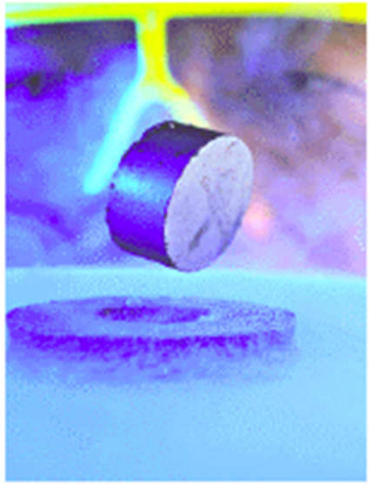
electrical resistance (1911)



field expulsion (1933)
Meissner-Ochsenfeld effect



H. Kamerling-Onnes

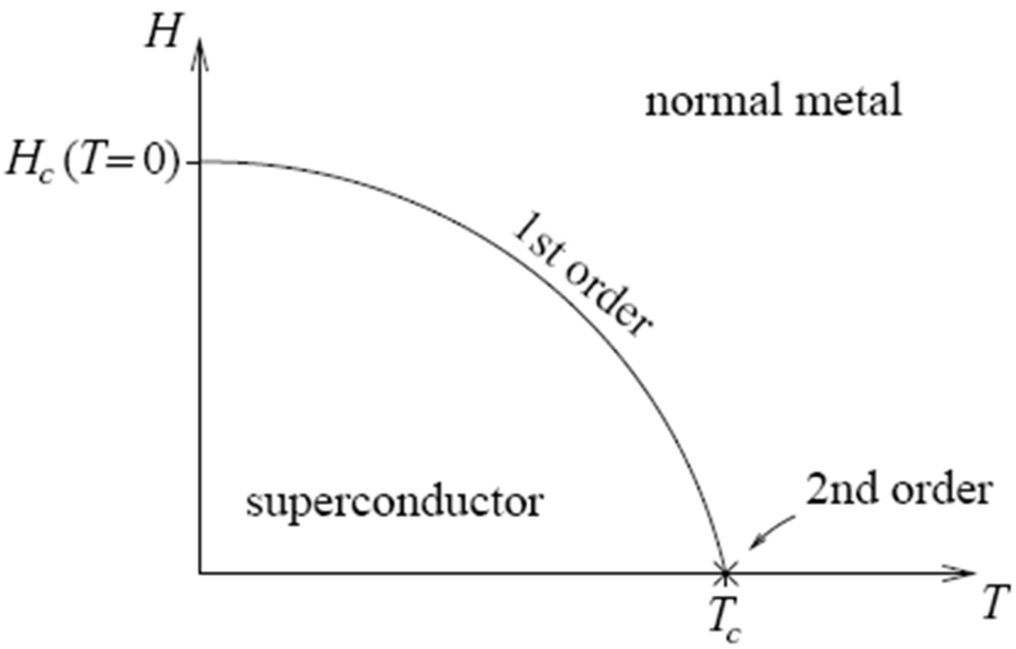


W. Meissner

Type I superconductor

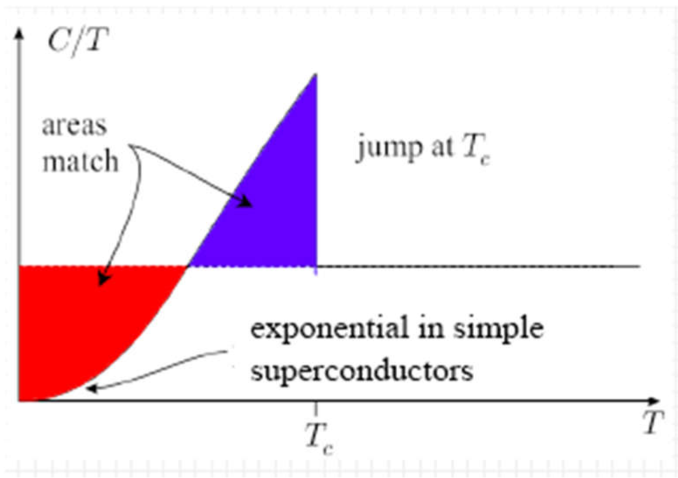
- Superconductivity is a thermodynamic phase

B = 0 inside for B < B_c (Meißner phase)

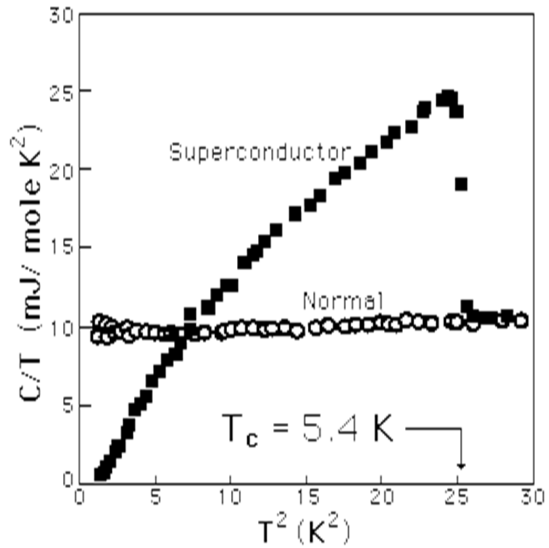


Thermodynamics: specific heat

Electronic specific heat around superconducting transition



Vanadium

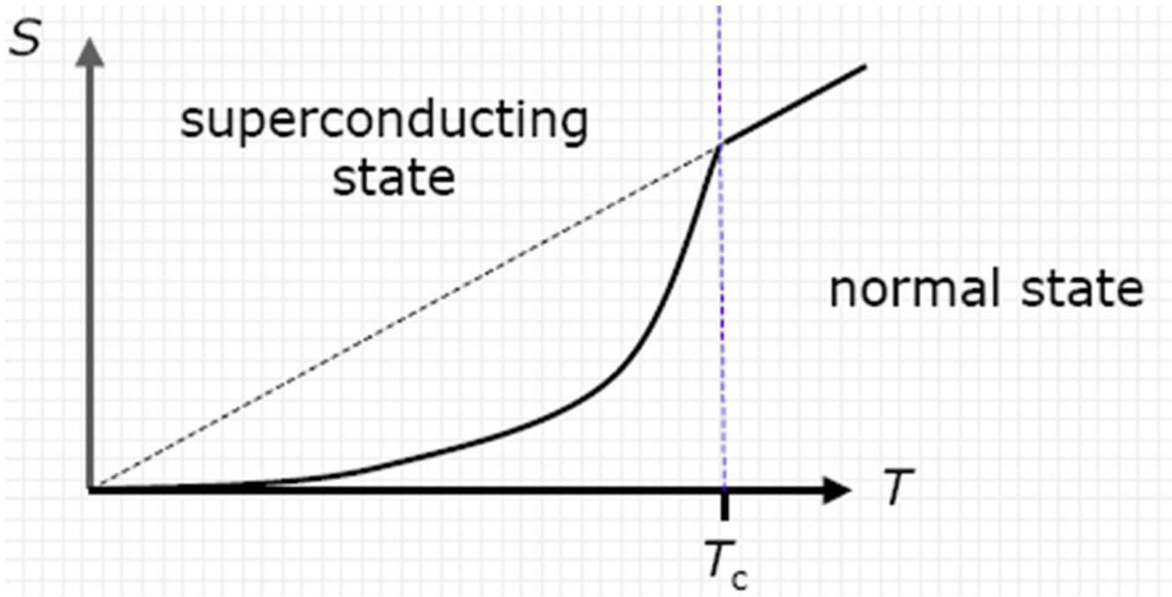


- **exponential low T behavior in conventional sc (BCS)**
  power law low T behavior in unconventional sc

- **matching areas → entropy conserved at T_C**
  consistent with second order phase transition

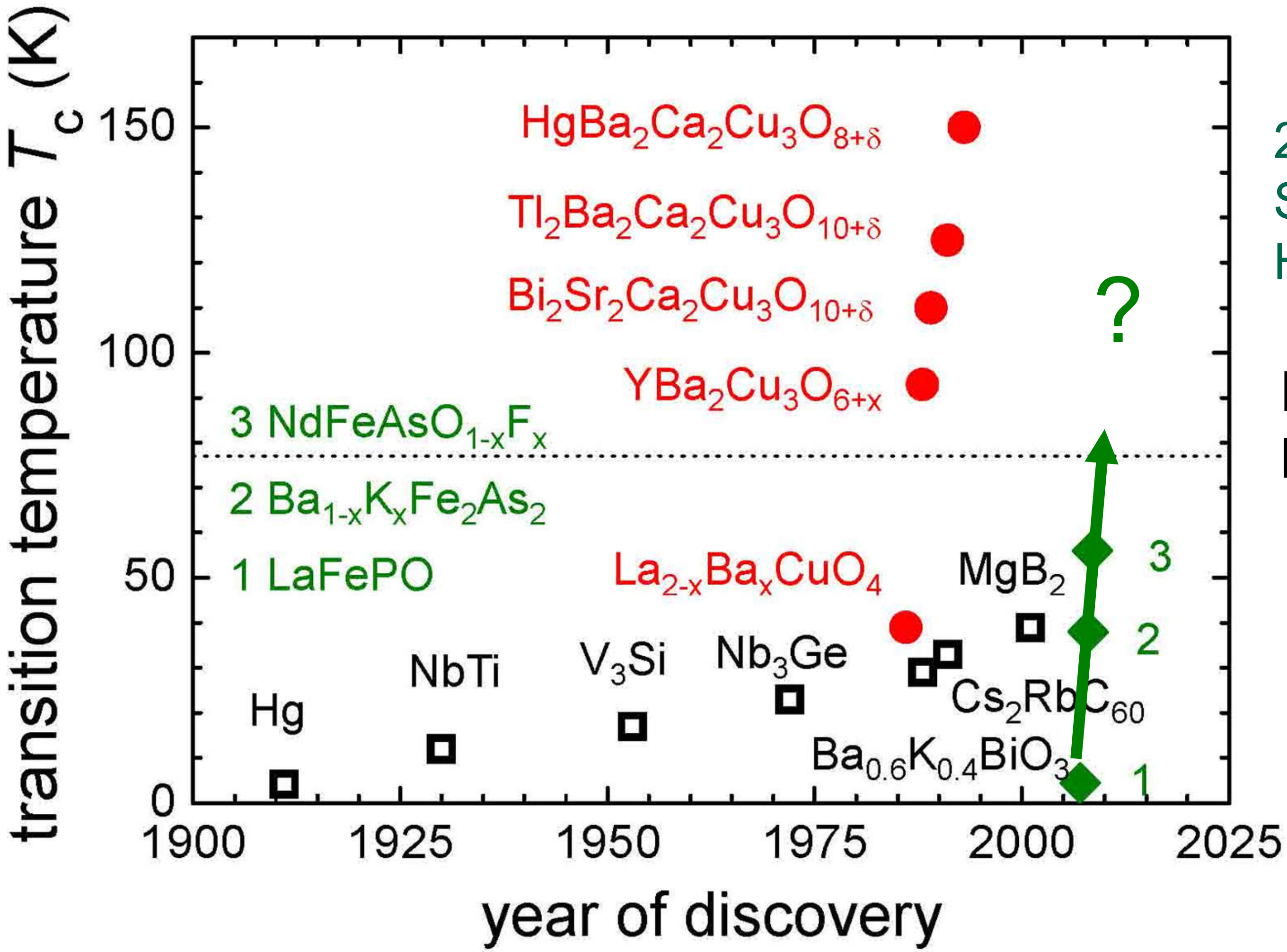
Thermodynamics: entropy

Entropy S versus temperature



- **Superconducting state is the more ordered state**
- **Description using the concept of an order parameter useful**
  → Ginzburg-Landau theory

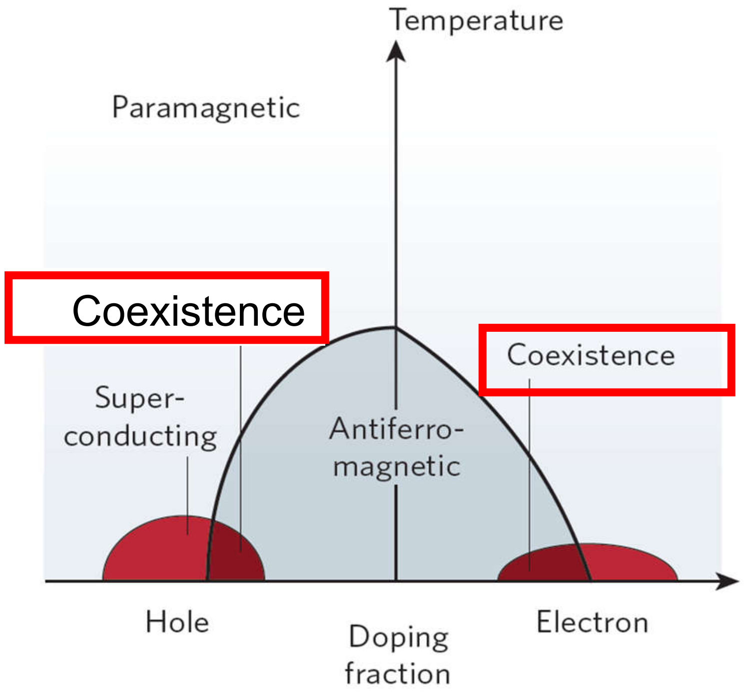
1986 Cuprate high-T_C



2007 Fe-based Superconductors Hosono et al.

Liquid nitrogen boiling temp

Coexistence of Superconductivity and Magnetic Order



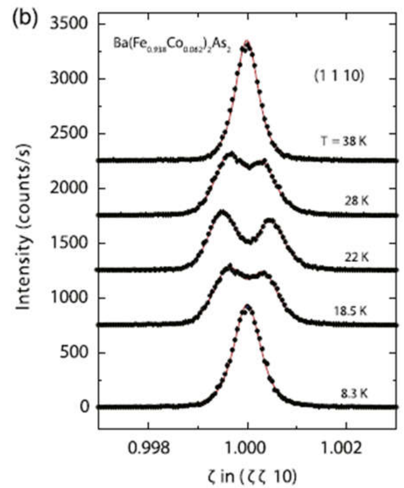
$Ba_{1-x}K_xFe_2As_2$ $BaFe_{2-x}Co_xAs_2$

Critical evidence for coexistence:

- Bulk magnetic order
- Bulk superconductivity
- Coupling of order parameters

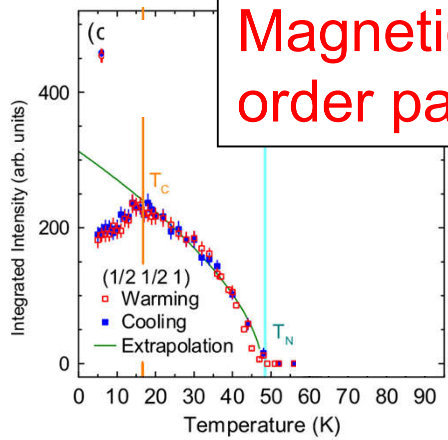
E. Wiesenmayer et al., Phys. Rev. Lett. **107,** 237001 (2011)
T. Goltz et al, Phys. Rev. B **89**, 144511 (2014)
Ph. Materne et al., Phys. Rev. B **92**, 134511 (2015)

Structural order parameter



Nandi et al., PRL 2010

Magnetic order parameter



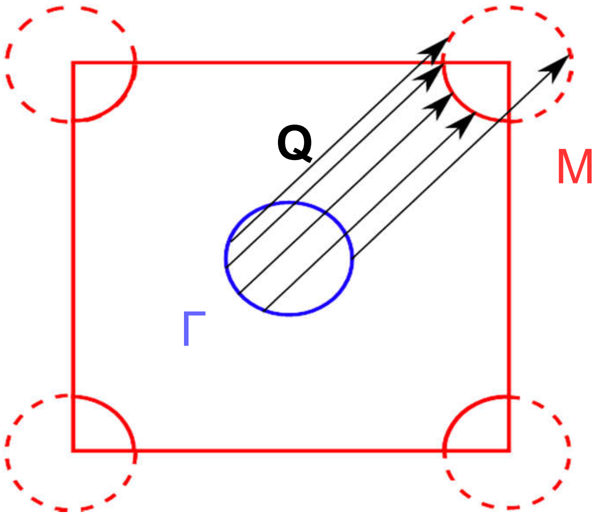
D.K. Pratt et al., PRL ´09

Electronic Instabilities

Competition for free electrons on the Fermi surface

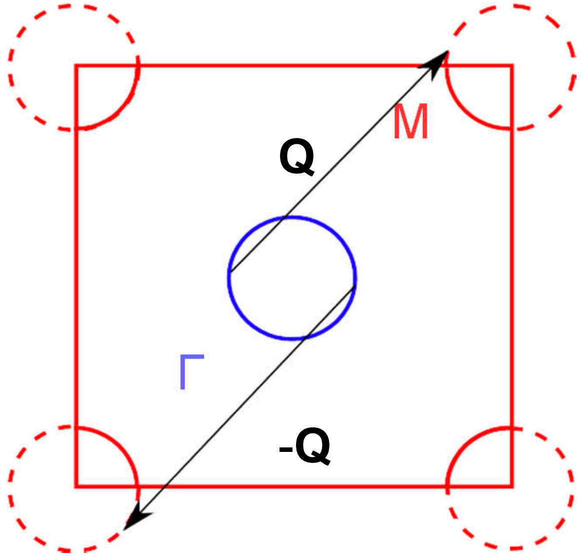
SDW magnetism

Resonant single electron scattering
on the Fermi surface
with nesting vector Q



Superconductivity

Resonant electron pair scattering
on the Fermi surface
with nesting vector Q



Susceptibilites depend differently
on details of the Fermi surfaces (size, shape,…)

Landau-Theory for coupled order parameters

$$F[\psi,\vec{M}] = \int \mathrm{d}^3r \left\{ \frac{\alpha}{2}|\psi(\vec{r})|^2 + \frac{\beta}{4}|\psi(\vec{r})|^4 + \frac{\gamma}{2}|\vec{\nabla}\psi(\vec{r})|^2 + \frac{d}{2}|\psi(\vec{r})|^2|\vec{M}(\vec{r})|^2 \right.$$
$$\left. + \frac{a}{2}|\vec{M}(\vec{r})|^2 + \frac{b}{4}|\vec{M}(\vec{r})|^4 + \frac{g}{2}|\vec{\nabla}\vec{M}(\vec{r})|^2 \right\}$$

Magnetism and superconductivity compete for the same electrons at the Fermi surface → d positive

Conditions for non-zero order parameters

$$a = a_0[T - T_{\mathrm{N}0}] \quad , \; a_0 > 0$$
$$\alpha = \alpha_0[T - T_{\mathrm{c}0}] \quad , \; \alpha_0 > 0$$

$$|\psi|^2 = -\frac{\alpha b - ad}{b\beta - d^2} \quad , \; \alpha b < ad$$
$$\vec{M}^2 = -\frac{a\beta - \alpha d}{b\beta - d^2} \quad , \; a\beta < \alpha d$$

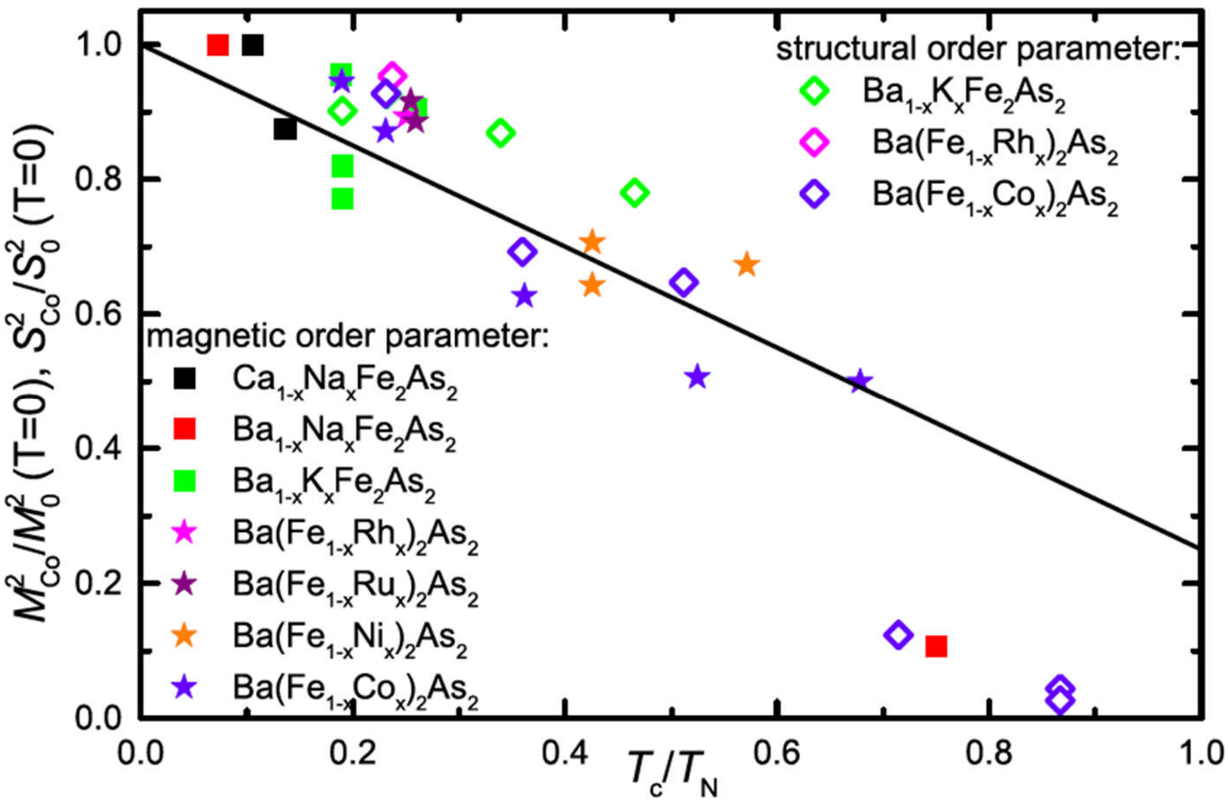
→Linear suppression of the magnetic order parameter as a function of the ratio of the critical temperatures T_C / T_N

$$m_{\mathrm{red}} = \frac{\vec{M}^2_{\mathrm{co}}}{\vec{M}^2_0}(T=0) = 1 - \underbrace{\frac{d}{a_0}\frac{\alpha_0 b - a_0 d}{b\beta - d^2}}_{\Delta m(d)}\frac{T_{\mathrm{c}}}{T_{\mathrm{N}}}$$

Ph. Materne et al., Phys. Rev. B (2015)

Universal suppression of magnetic order parameter

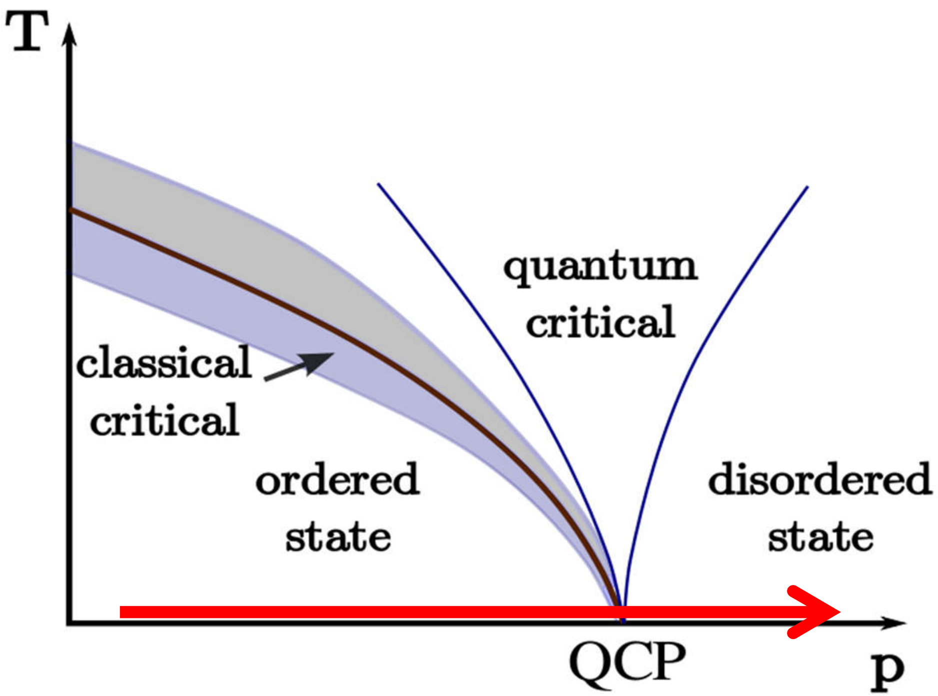
$$m_{\text{red}} = \frac{\vec{M}_{\text{co}}^2}{\vec{M}_0^2}(T=0) = 1 - \underbrace{\frac{d}{a_0}\frac{\alpha_0 b - a_0 d}{b\beta - d^2}}_{\Delta m(d)}\frac{T_c}{T_N}.$$

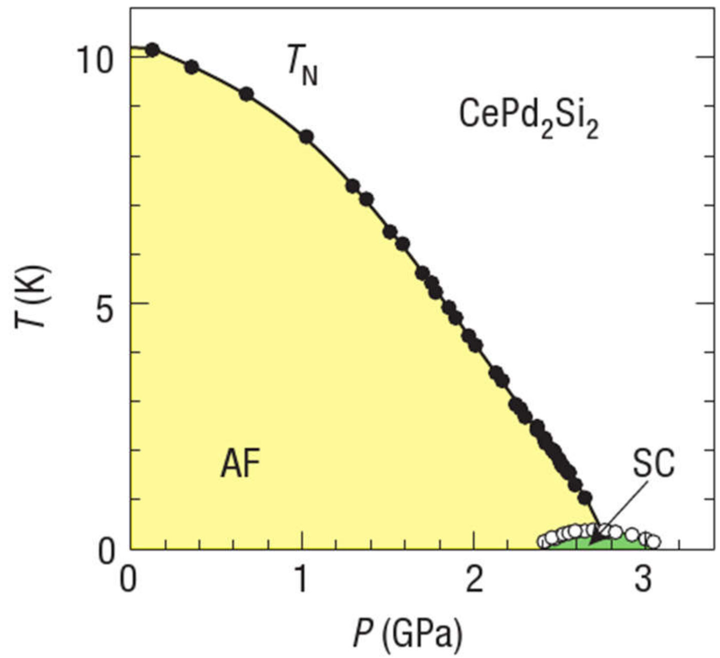


Ph. Materne et al., Phys. Rev. B (2015)

Quantum Phase transitions

- What happens, when for a continuous phase transition T_C is suppressed to zero temperature via some external parameter p ?
  Critical temperature becomes quantum critical point (QCP)
- What destroys the ordered state at T→0 as a function of p?
  Enhanced quantum critical fluctuations, e.g. antiferromagnetic spin fluctuations
- Often new order emerges driven by these quantum fluctuations, e.g. superconductivity





Mathur et al., Nature 1998

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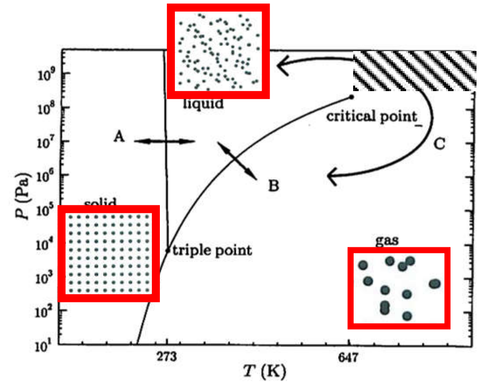

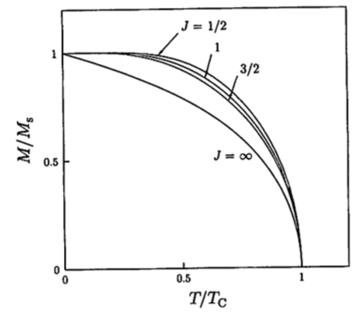

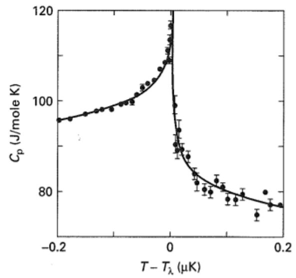

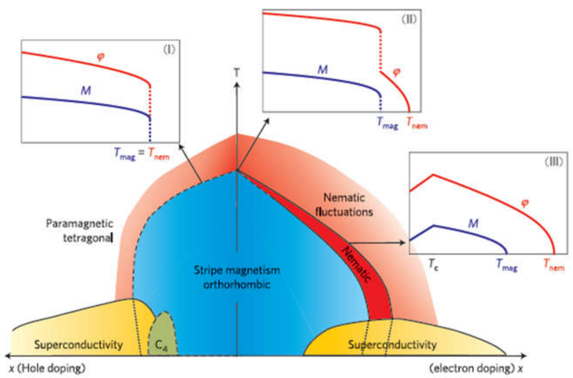

Ginzburg-Landau

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