

27. Phase Transitions

Jan. 27, 2020

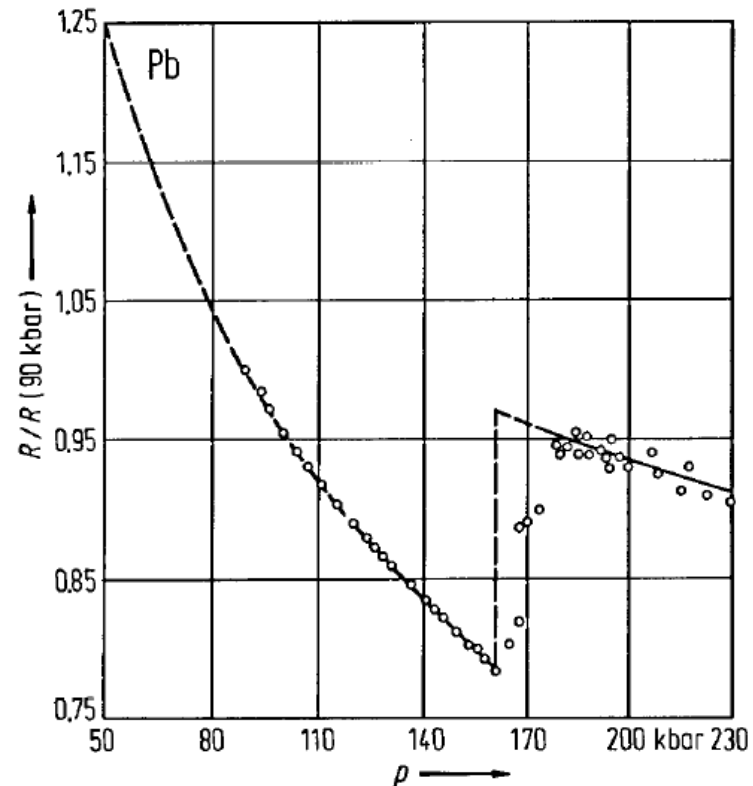
Strain

Strain displaces the atoms and the band structure needs to be recalculated.

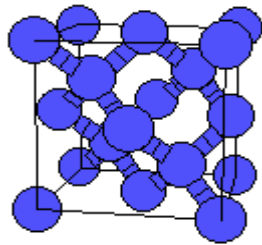
This changes the density of states and the thermodynamic properties.

Make Legendre transformations from the internal energy to the enthalpy that has temperature and pressure as independent variables. The crystal structure with lowest enthalpy will be observed.

Enthalpy is calculated from the microscopic states of electrons and phonons.

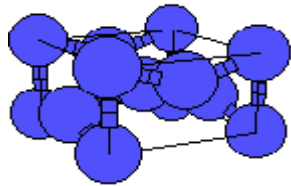


Structural phase transitions in Si



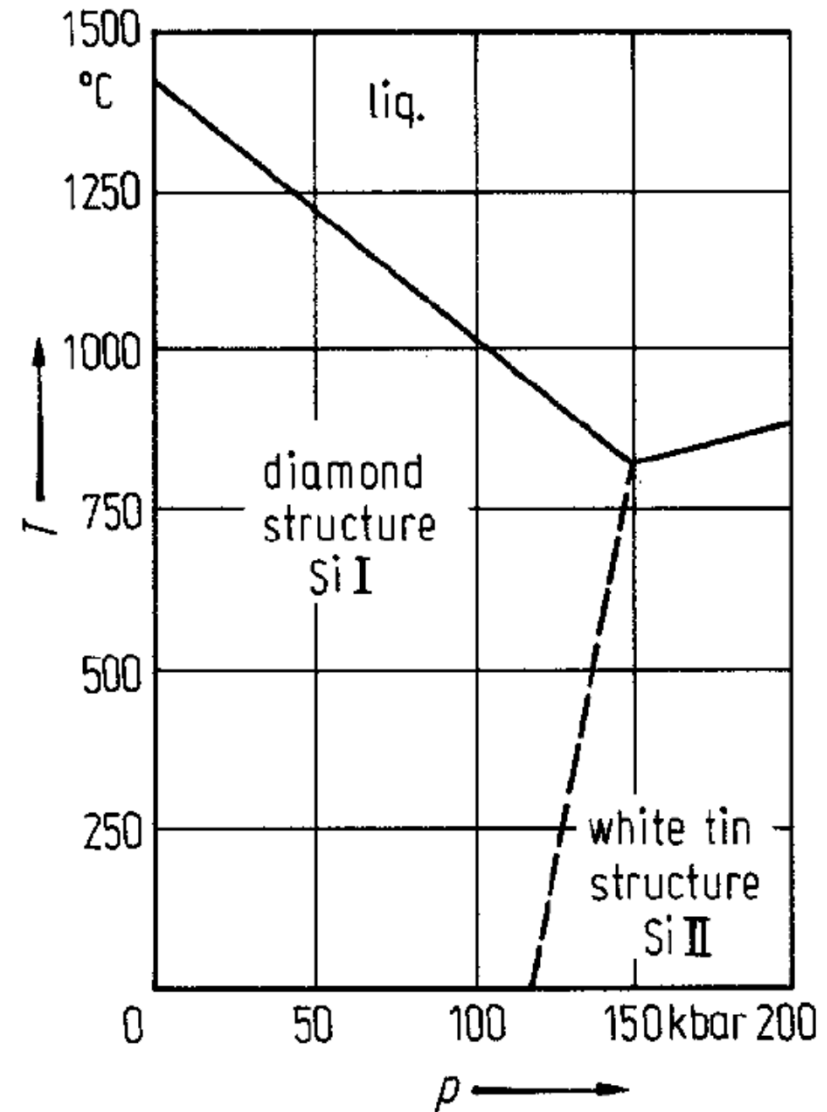
α -Sn, gray tin, diamond

transition at 13 C

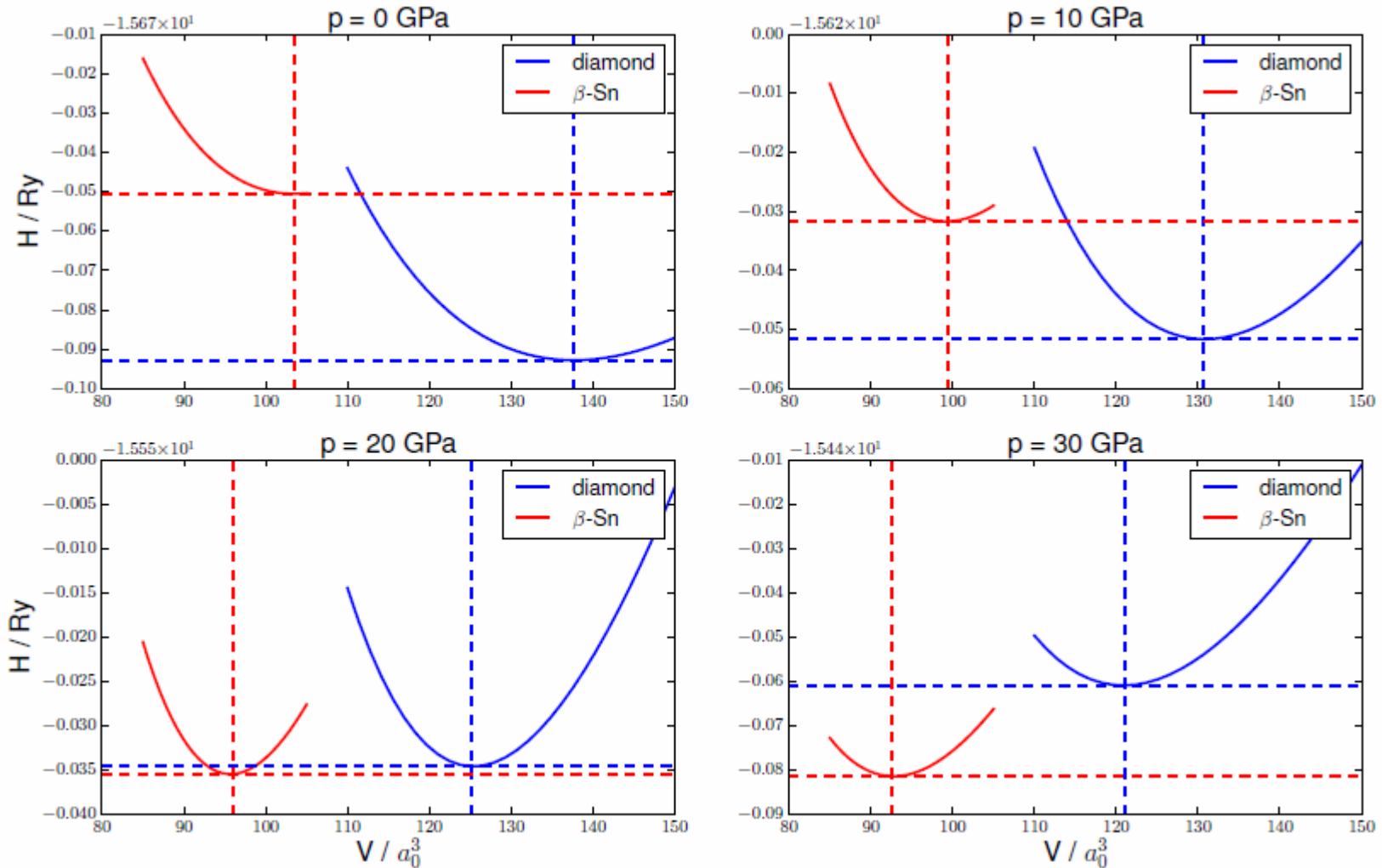


β -Sn, white tin, tetragonal

silicon makes a diamond to β -Sn transition under pressure



Structural phase transition in Si



Michael Scherbela 2015

Structural phase transition in Si

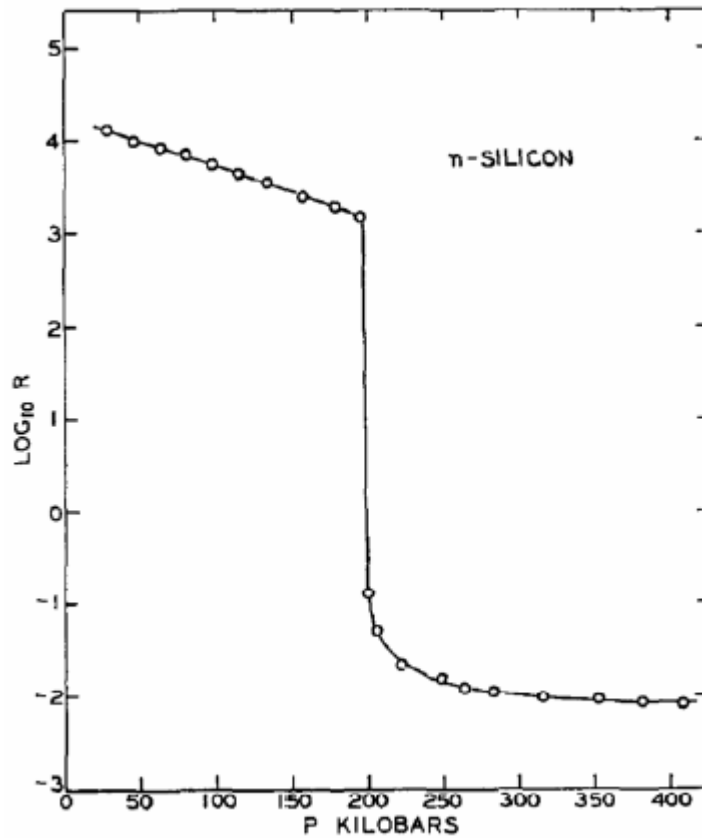
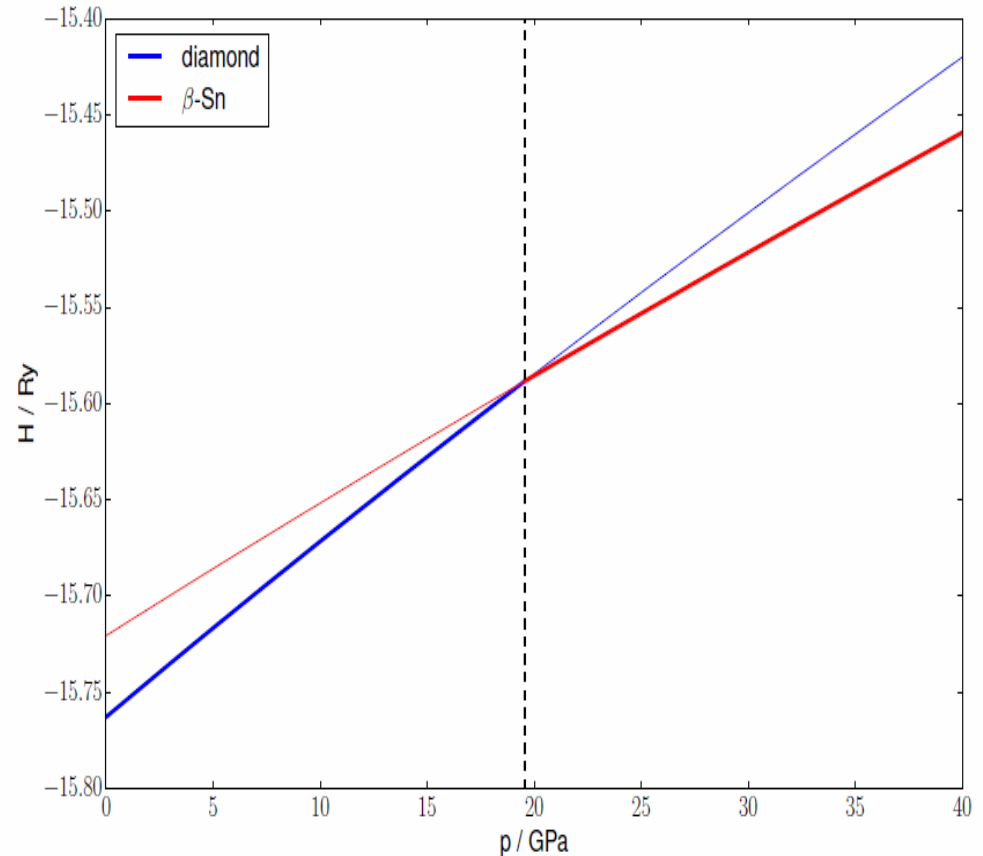


FIG. 1. Resistance vs. pressure—*n*-Silicon.



200 kbar = 20 GPa

Michael Scherbela 2015

H. G. D. S. Minomura, "Pressure induced phase transitions in silicon, germanium and some iii-v compounds," *J. Phys. Chem. Solids Pergamon Press*, vol. 23, pp. 451–456, 1962.

The surprising role of magnetism on the phase stability of Fe (Ferro)

1. Introduction

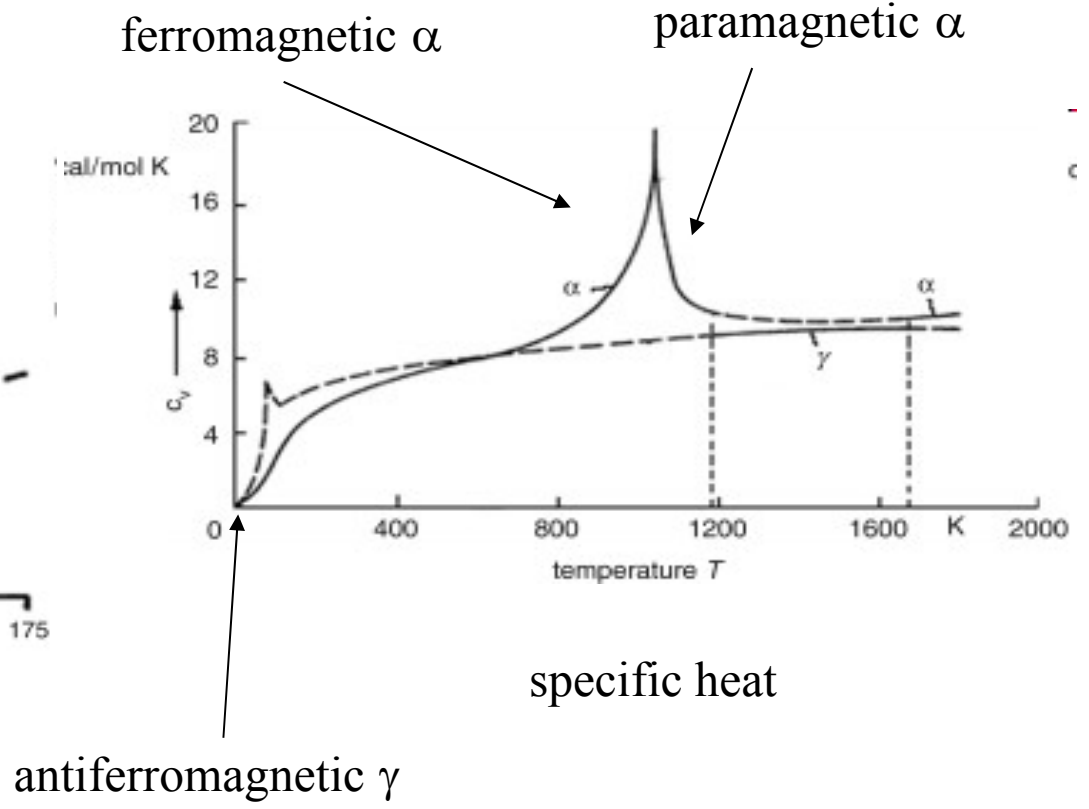
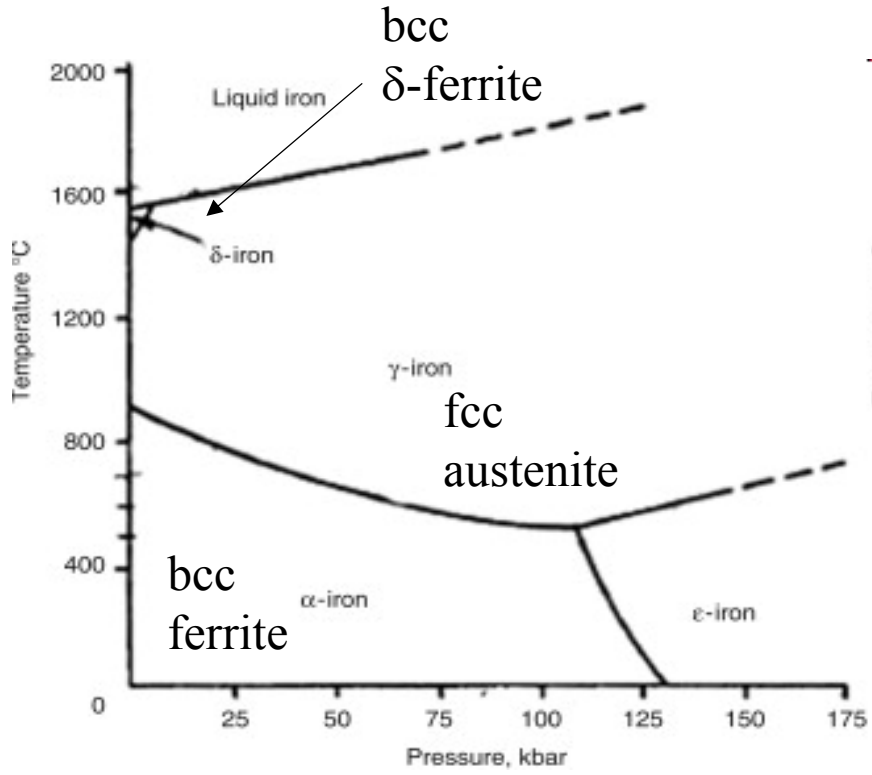
The phase stability of many elements shows the following pattern:

1. A low enthalpy is mainly responsible for the choice of structure at low temperatures.
2. At higher temperatures, structures (phases) are stable which have higher entropies.

This often translates into the low temperature phase being a close packed one and the high temperature phase having a more open structure, that is, a less close packed structure. For example, the low temperature phase of Ti is close packed hexagonal (HCP) while the high temperature phase is BCC.

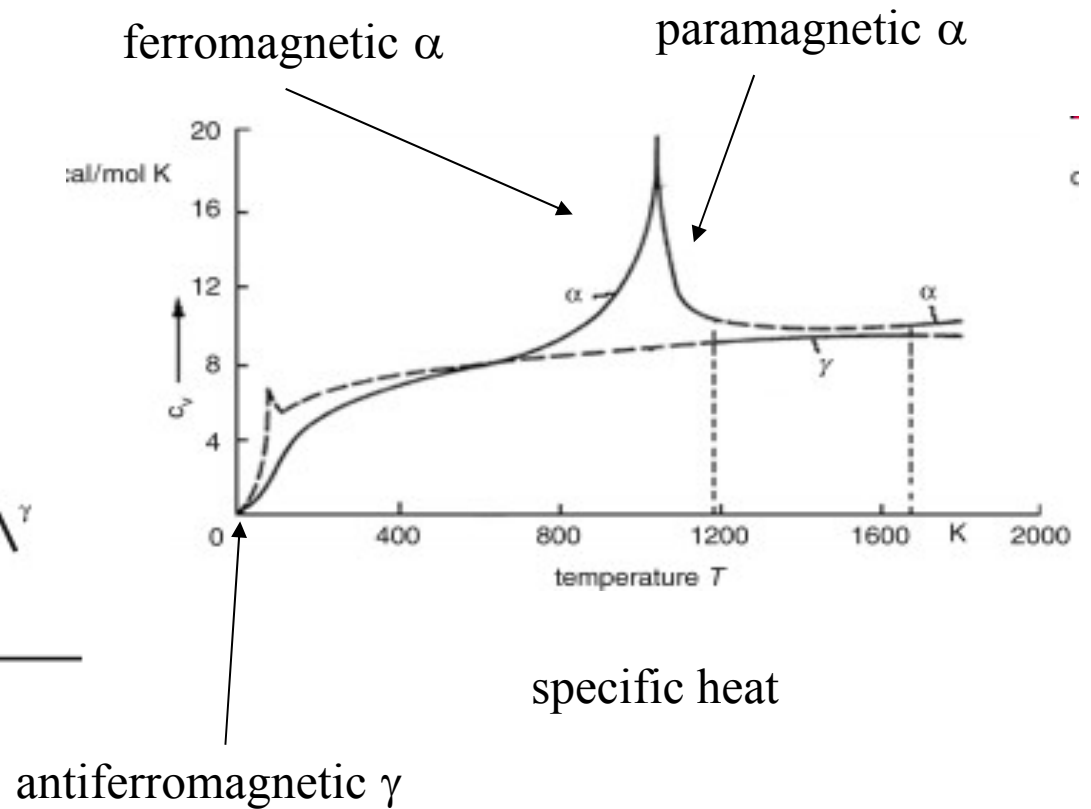
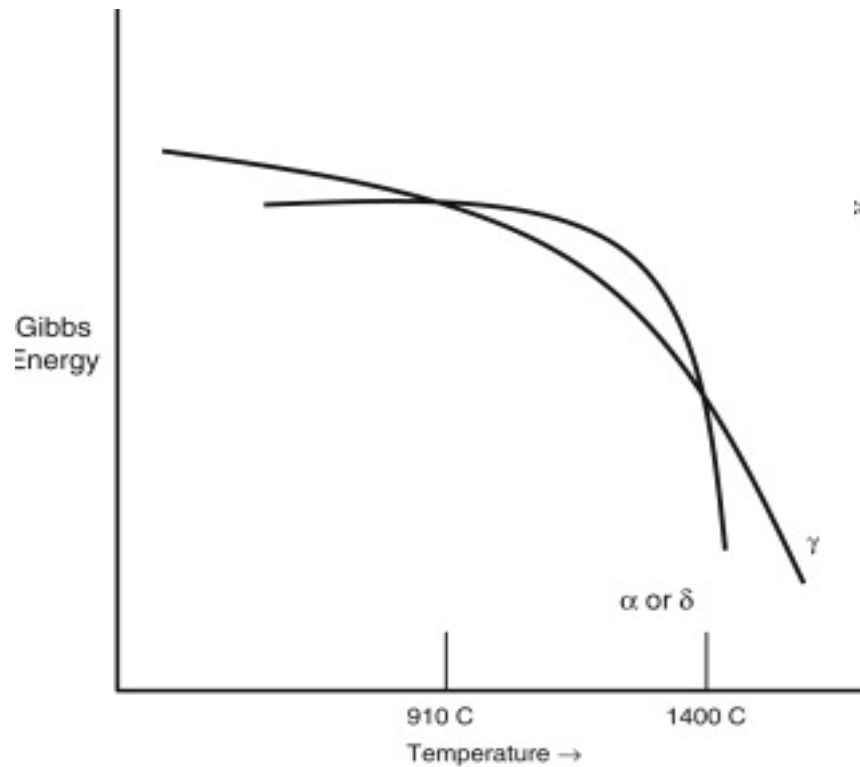
$$G = U + pV - TS$$

Structural phase transitions in iron



doi:10.1016/j.calphad.2008.07.009

Structural phase transitions in iron



doi:10.1016/j.calphad.2008.07.009

Iron alloy phases

Ferrite (α -iron, δ -iron)

Austenite (γ -iron)

Pearlite (88% ferrite, 12% cementite)

Martensite

Bainite

Ledeburite (austenite-cementite eutectic, 4.3% carbon)

Cementite (iron carbide, Fe_3C)

Beta ferrite (β -iron)

Hexaferrum (ϵ -iron)

Steel classes

Crucible steel

Carbon steel ($\leq 2.1\%$ carbon; low alloy)

Spring steel (low or no alloy)

Alloy steel (contains non-carbon elements)

Maraging steel (contains nickel)

Stainless steel (contains $\geq 10.5\%$ chromium)

Weathering steel

Tool steel (alloy steel for tools)

Other iron-based materials

Cast iron ($> 2.1\%$ carbon)

Ductile iron

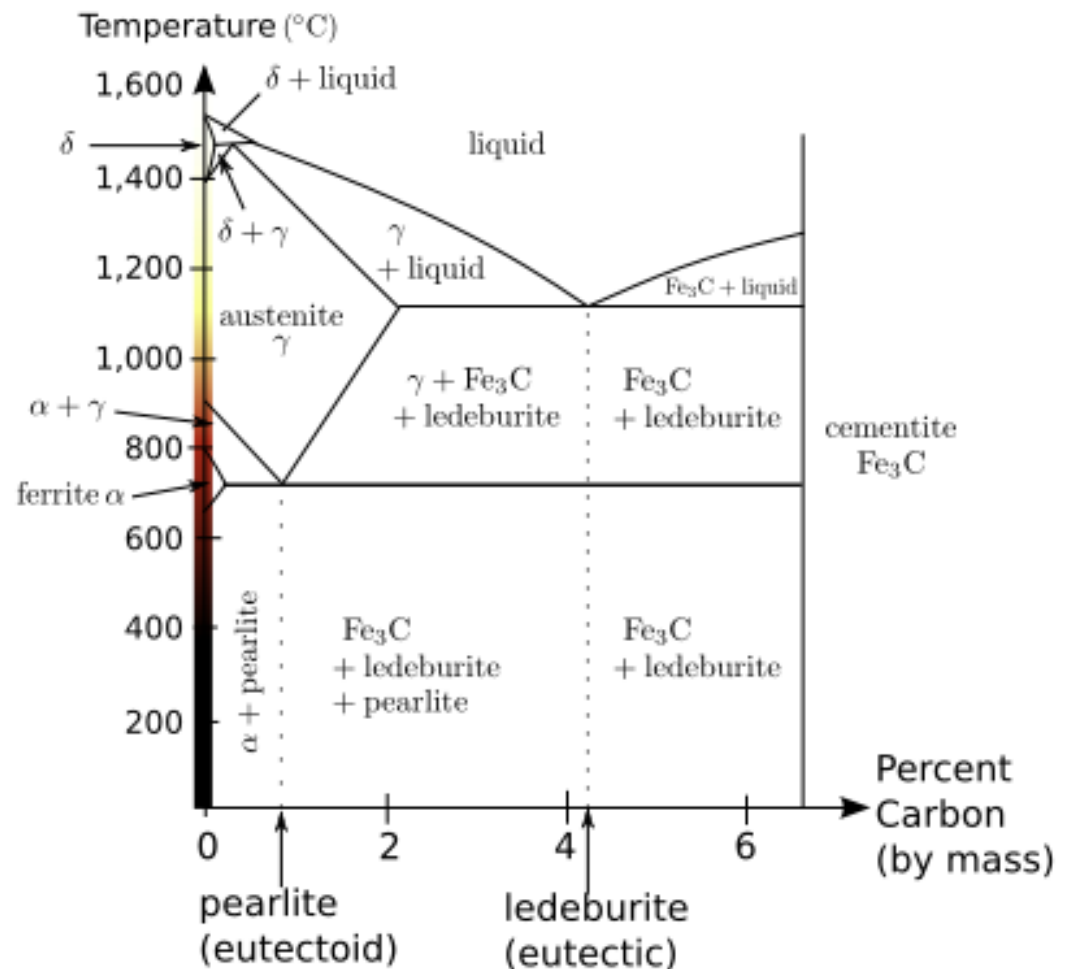
Gray iron

Malleable iron

White iron

Wrought iron (contains slag)

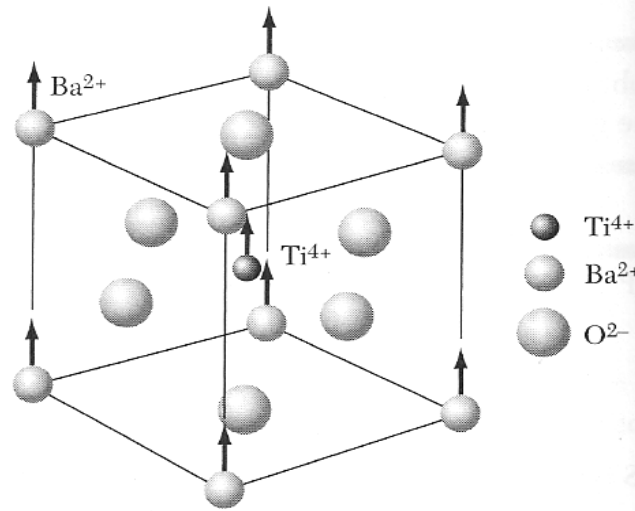
v · d · e



Ferroelectricity

Ferroelectricity

ABX₃
Perovskites

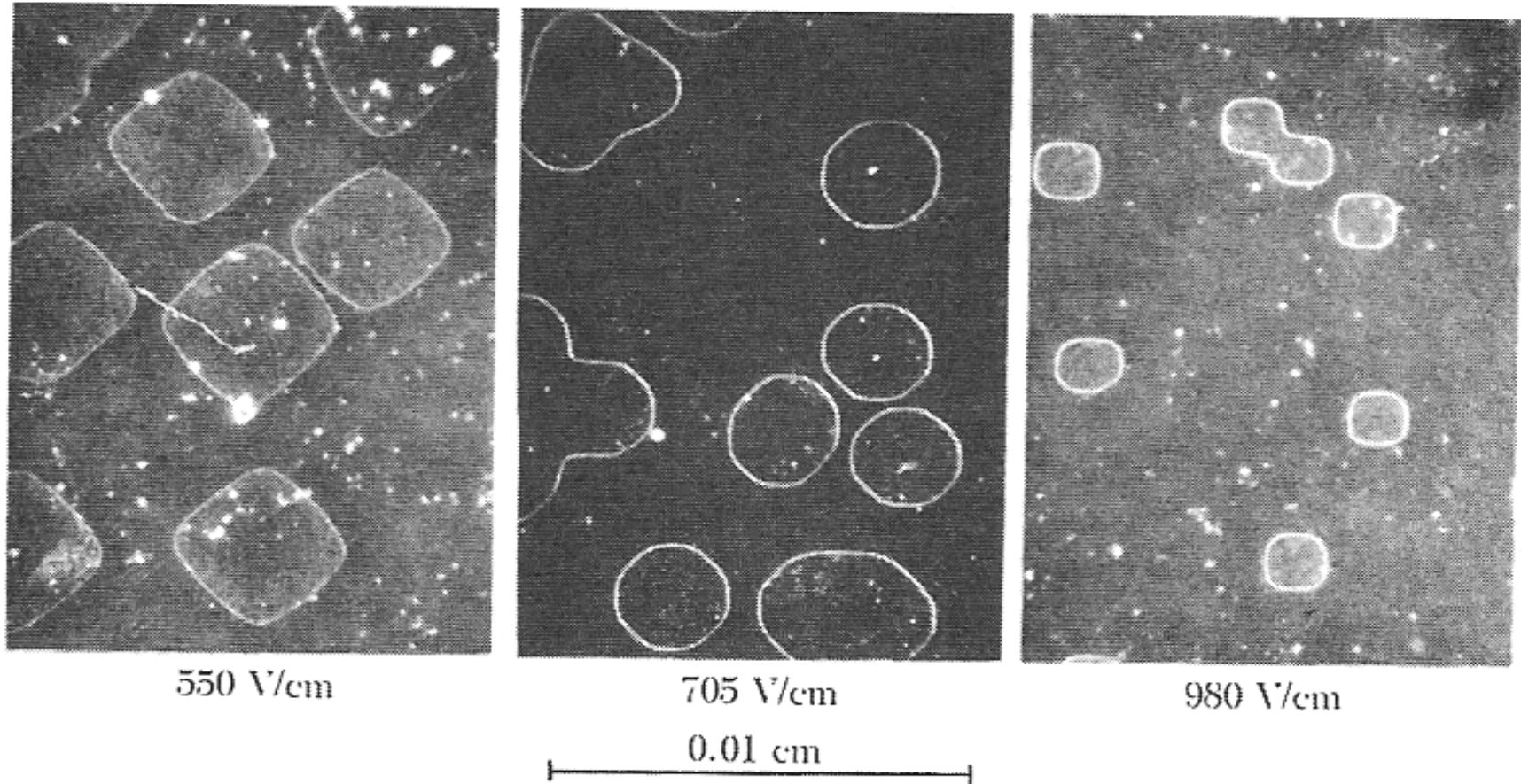


Spontaneous polarization
 Analogous to ferromagnetism
 Structural phase transition
 T_c is transition temperature

Electric field inside the material,
 is not conducting

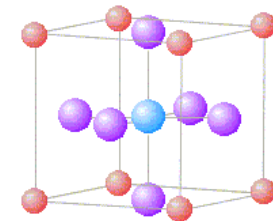
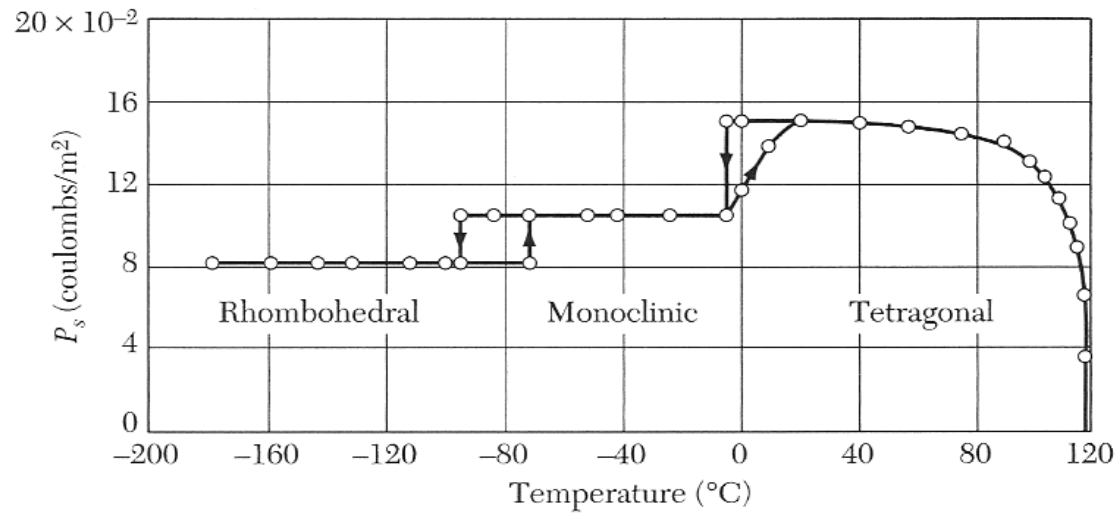
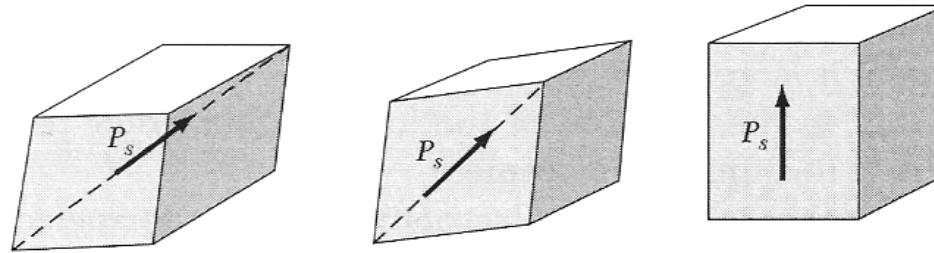
		T_c , in K	P_s , in $\mu\text{C cm}^{-2}$, at T K	
KDP type	KH ₂ PO ₄	123	4.75	[96]
	KD ₂ PO ₄	213	4.83	[180]
	RbH ₂ PO ₄	147	5.6	[90]
	KH ₂ AsO ₄	97	5.0	[78]
	GeTe	670	—	—
TGS type	Tri-glycine sulfate	322	2.8	[29]
	Tri-glycine selenate	295	3.2	[283]
Perovskites	BaTiO ₃	408	26.0	[296]
	KNbO ₃	708	30.0	[523]
	PbTiO ₃	765	>50	[296]
	LiTaO ₃	938	50	
	LiNbO ₃	1480	71	[296]

Ferroelectric domains



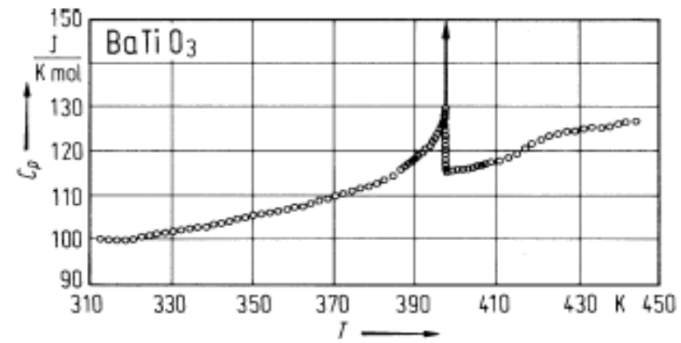
Increasing the electric field polarizes the material.

BaTiO₃



cubic (contains i = >
no spontaneous P)

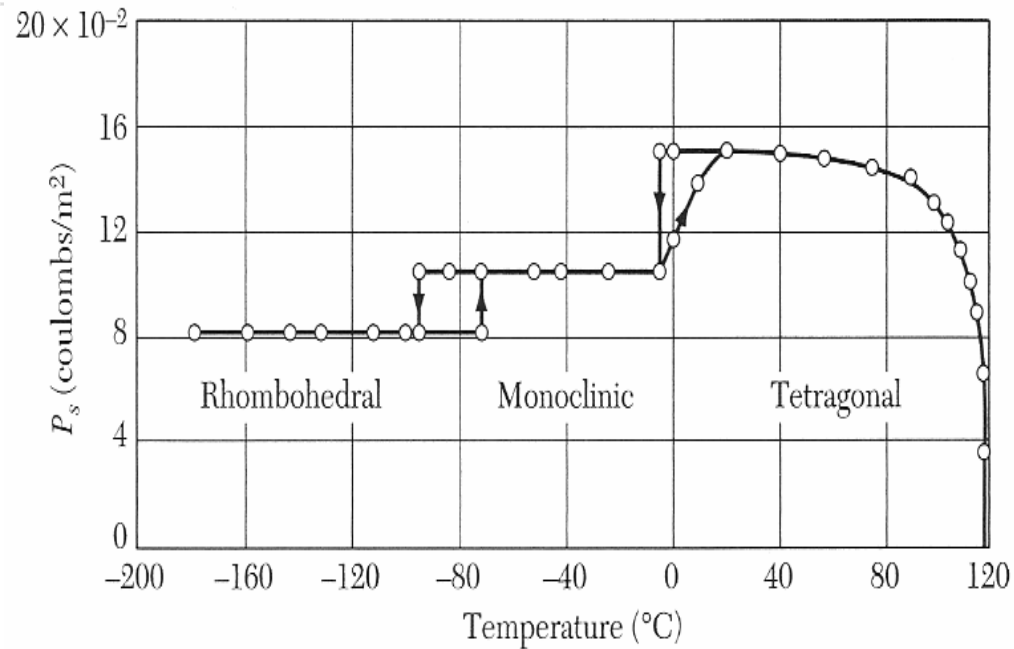
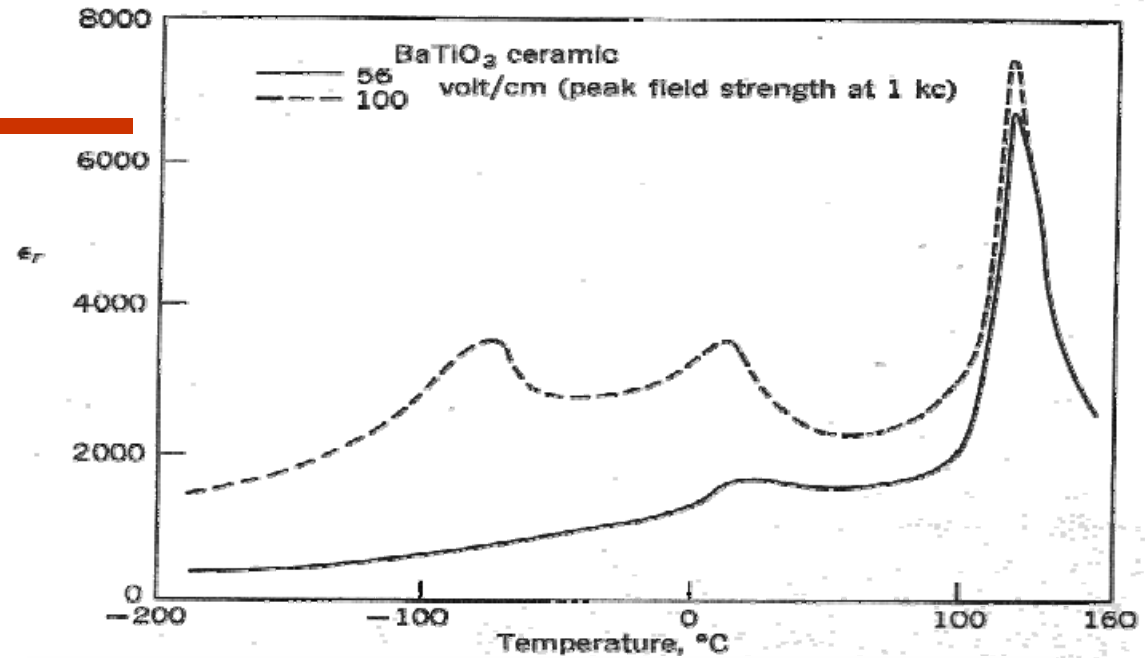
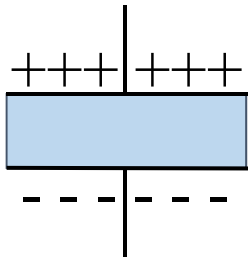
Can be used to make
nonvolatile memory



BaTiO₃

$$\epsilon_r = \chi + 1$$

Can be used to make
ultracapacitors

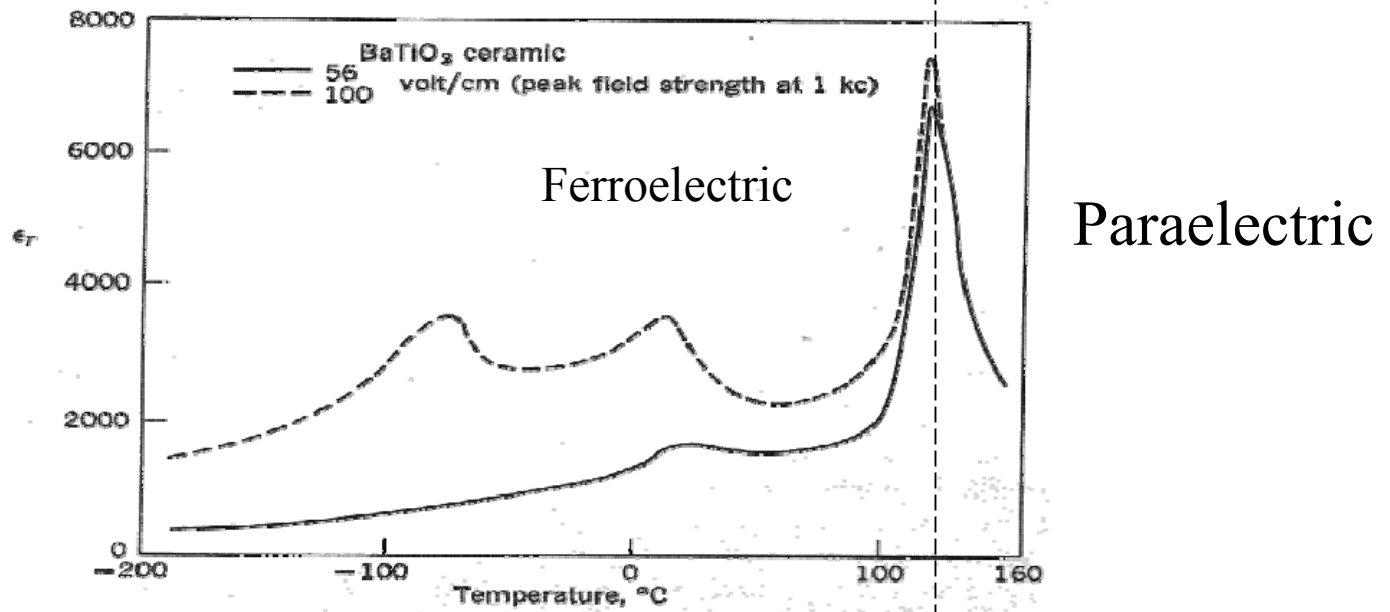


Paraelectric state

Above T_c , BaTiO₃ is paraelectric. The susceptibility (and dielectric constant) diverge like a Curie-Weiss law.

$$\chi \propto \frac{1}{T - T_c} \quad \epsilon = (1 + \chi) \epsilon_0$$

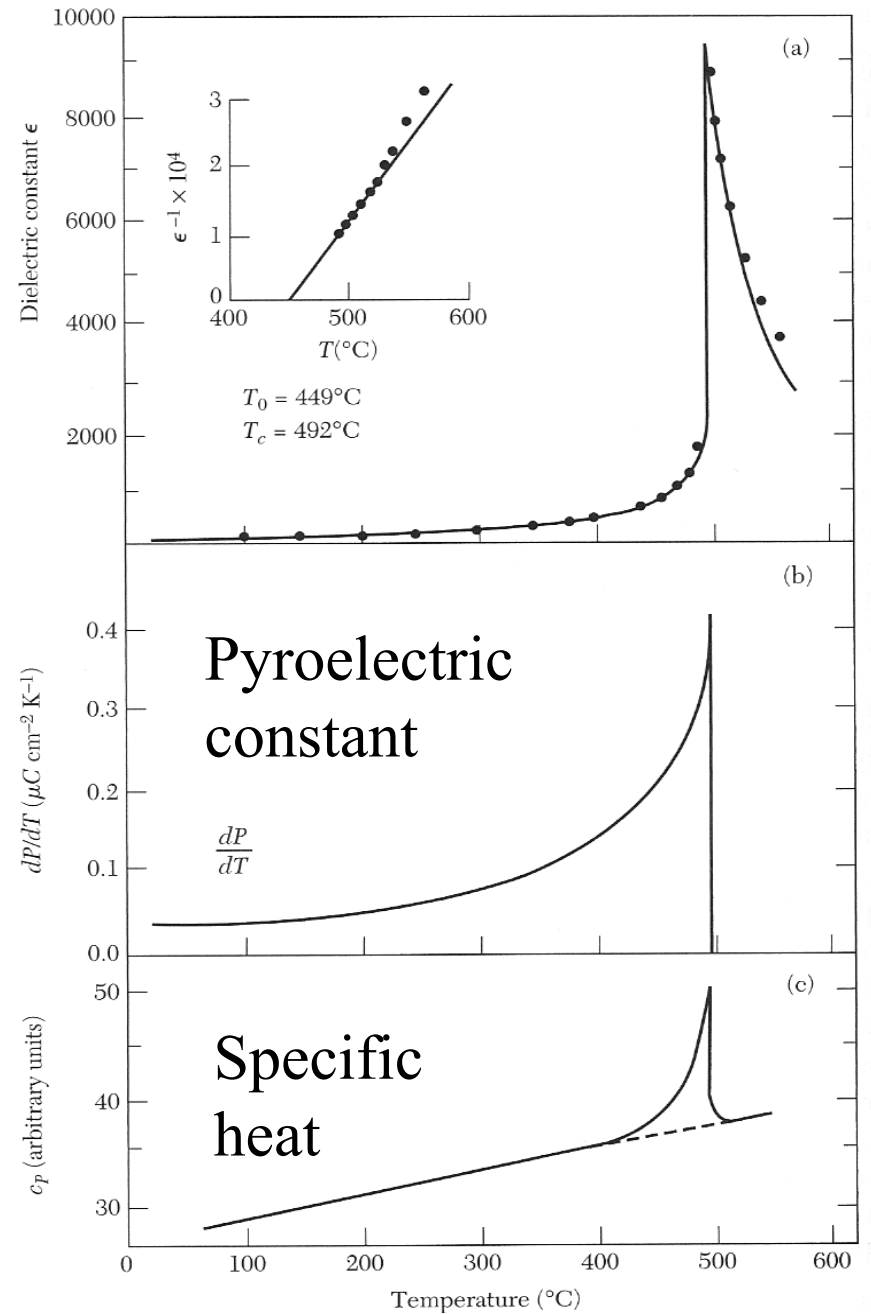
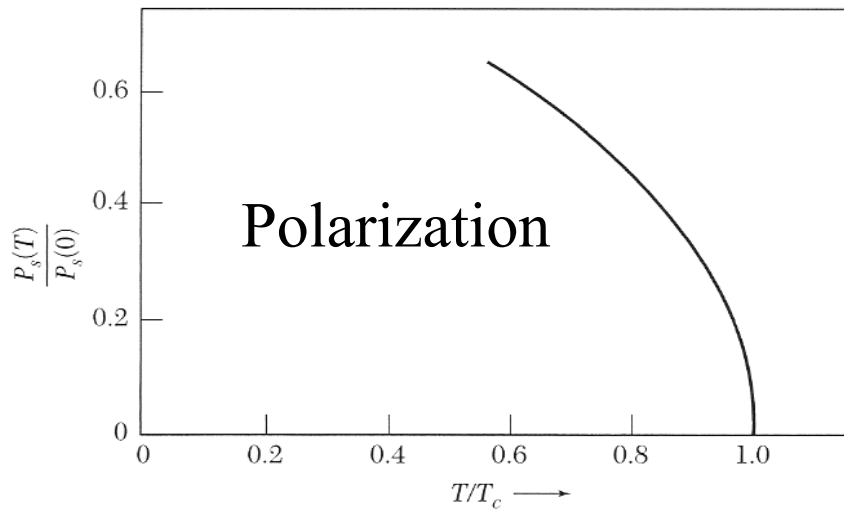
This causes a big peak in the dielectric constant at T_c .



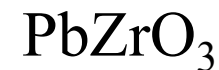
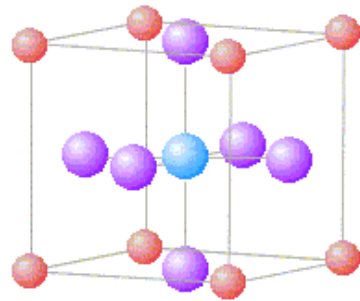
PbTiO₃

Dielectric constant

$$\epsilon \propto \frac{1}{T - T_c}$$



Antiferroelectricity

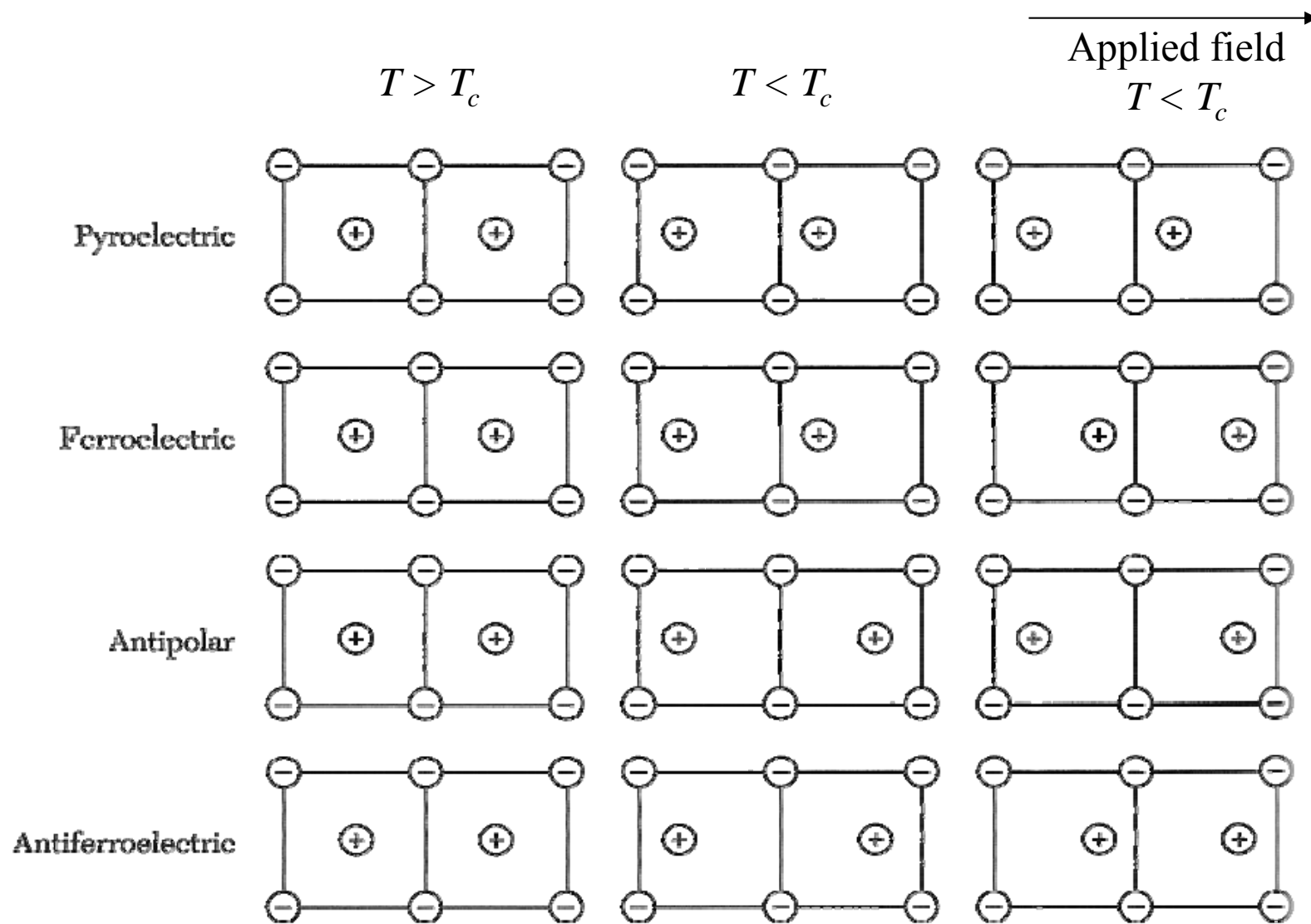


Polarization aligns antiparallel.

Associated with a structural phase transition.

Large susceptibility and dielectric constant near the transition.

Phase transition is observed in the specific heat, x-ray diffraction.



Piezoelectricity

Many ferroelectrics are piezoelectric.

Electric field couples to polarization, polarization couples to structure.

lead zirconate titanate ($\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ $0 < x < 1$)

—more commonly known as PZT

barium titanate (BaTiO_3) $T_c = 408 \text{ K}$

lead titanate (PbTiO_3) $T_c = 765 \text{ K}$

potassium niobate (KNbO_3) $T_c = 708 \text{ K}$

lithium niobate (LiNbO_3) $T_c = 1480 \text{ K}$

lithium tantalate (LiTaO_3) $T_c = 938 \text{ K}$

quartz (SiO_2), GaAs, GaN

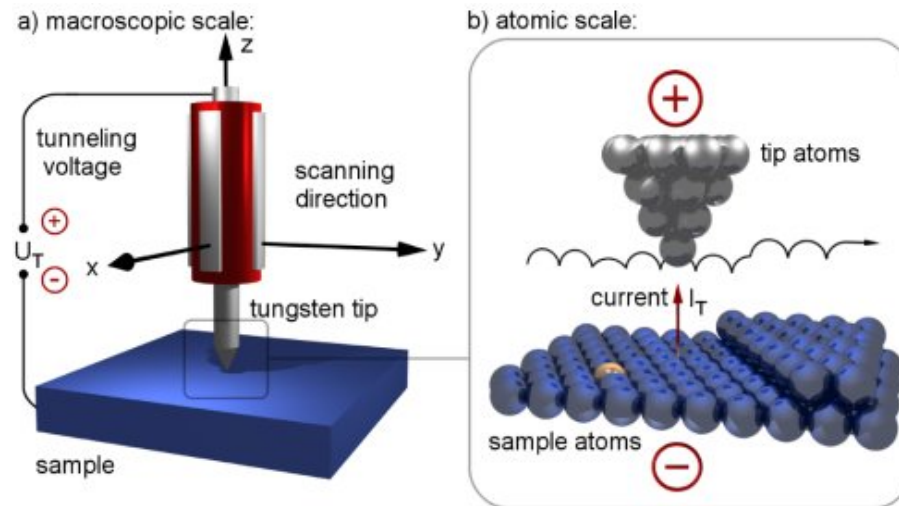
Gallium Orthophosphate (GaPO_4) $T_c = 970 \text{ K}$

Third rank tensor, No inversion symmetry

Piezoelectric crystal classes: 1, 2, m, 222, mm2, 4, -4, 422, 4mm, -42m, 3, 32, 3m, 6, -6, 622, 6mm, -62m, 23, -43m

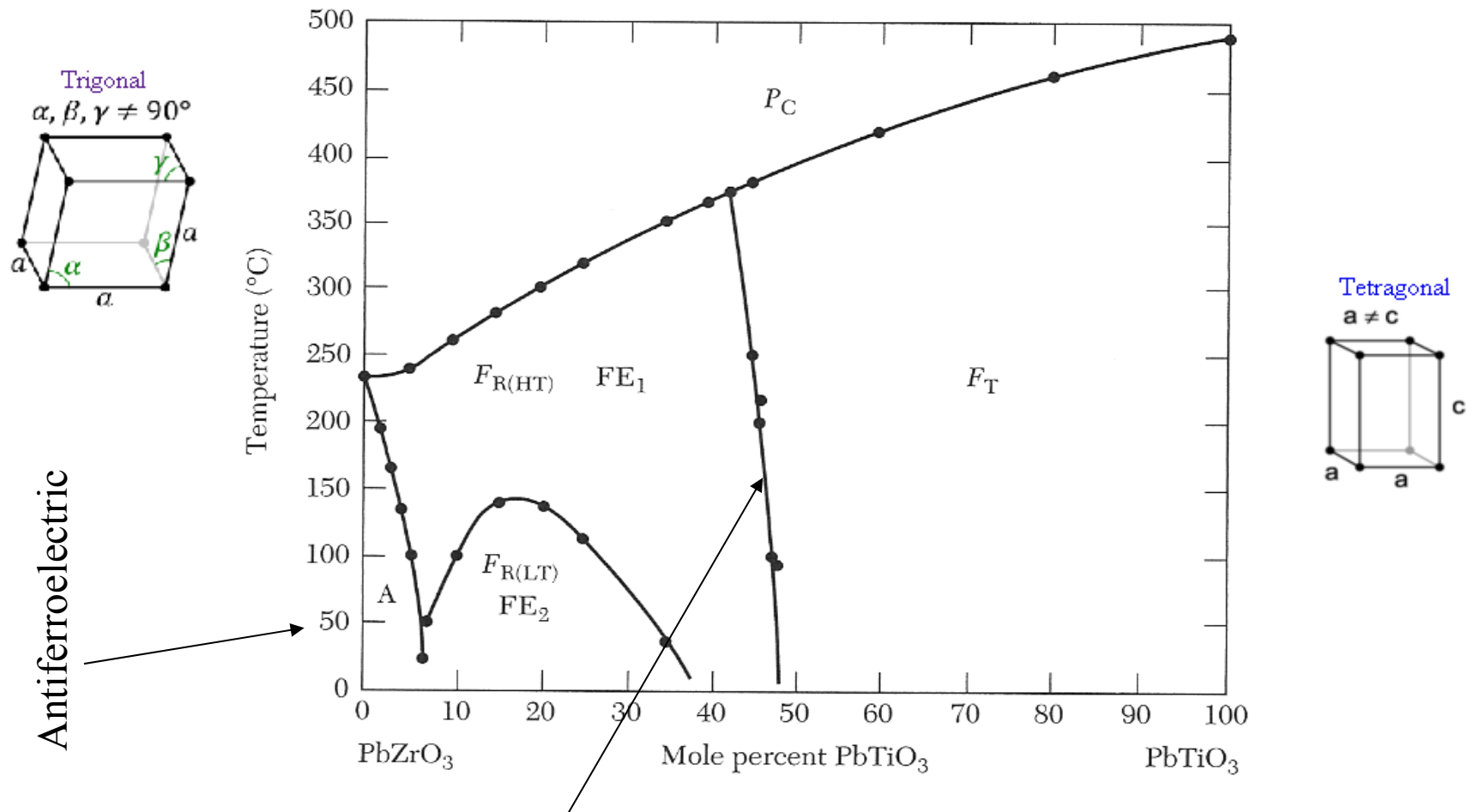
Piezoelectricity

When you apply a voltage across certain crystals, they get longer.



AFM's, STM's
Quartz crystal oscillators
Surface acoustic wave generators
Pressure sensors - Epcos
Fuel injectors - Bosch
Inkjet printers

PZT ($\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ $0 < x < 1$)



Large piezoelectric response near the rhombohedral-tetragonal transition.
Electric field induces a structural phase transition.

Nitinol

Ni Ti alloy

Shape memory: If it is bent below a certain transition temperature and then heated above that temperature, it returns to its original shape.

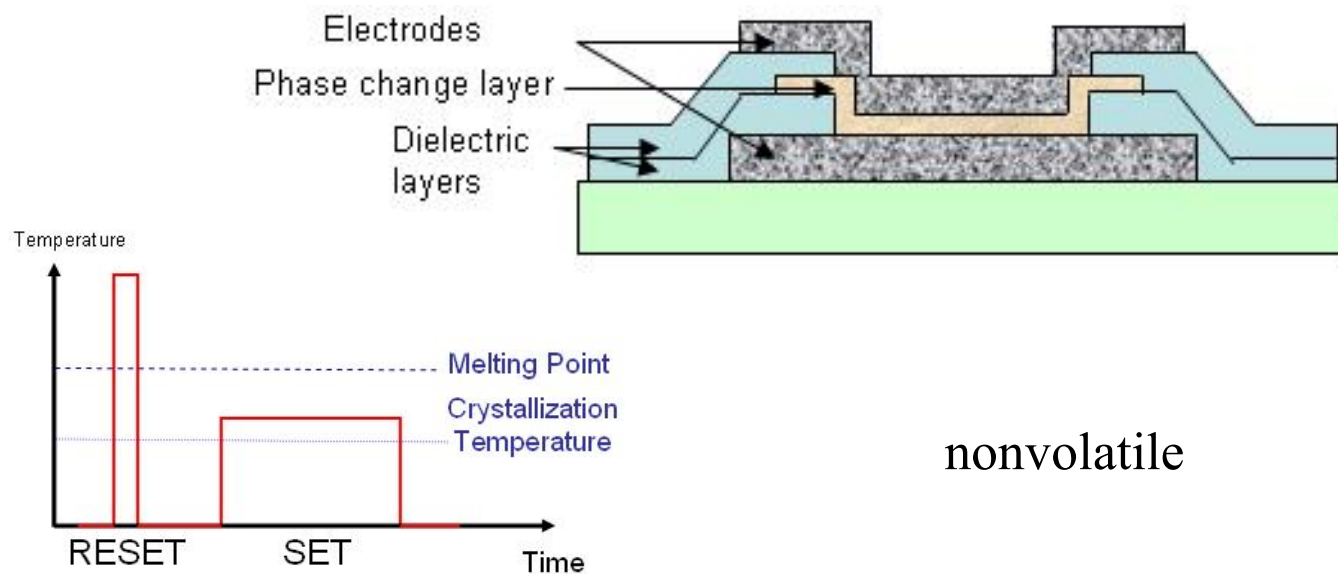
Superelasticity: Just above the transition temperature, the material exhibits elasticity 10-30 times that of an ordinary metal.

Martensite - Austenite

Phase change memory

Phase-change memory (PRAM) uses chalcogenide materials. These can be switched between a low resistance crystalline state and a high resistance amorphous state.

GeSbTe is melted by a laser in rewritable DVDs and by a current in PRAM.



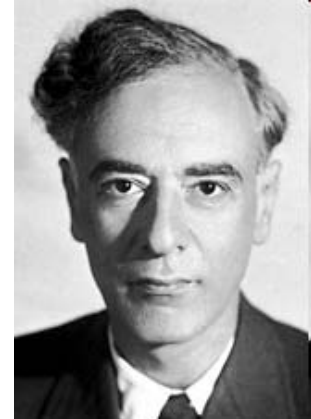
Landau Theory of Phase Transitions

Landau theory of phase transitions

A phase transition is associated with a broken symmetry.

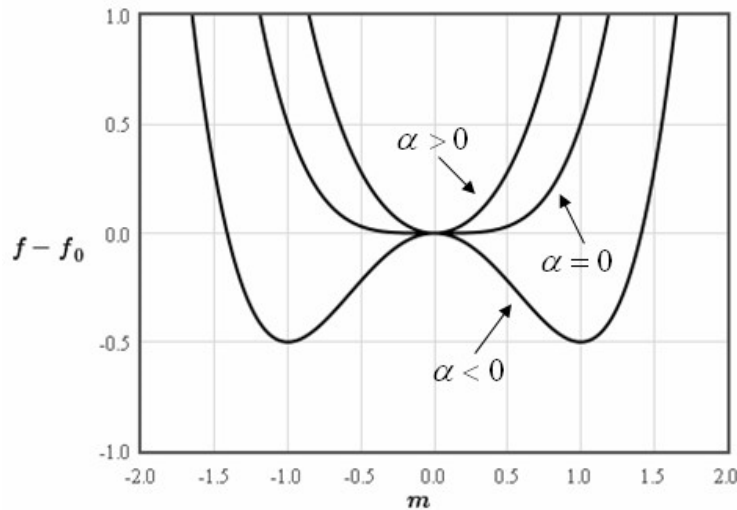
magnetism
cubic - tetragonal
water - ice
ferroelectric
superconductivity

direction of magnetization
different point group
translational symmetry
direction of polarization
gauge symmetry



Lev Landau

Temperature dependence of the order parameter



At $T = T_c$ $\alpha = 0$

Expand α in terms of $T - T_c$. Keep only the linear term. m and $T - T_c$ are both small near T_c .

$$f = f_0 + \alpha_0 (T - T_c) m^2 + \frac{1}{2} \beta m^4 + \dots$$

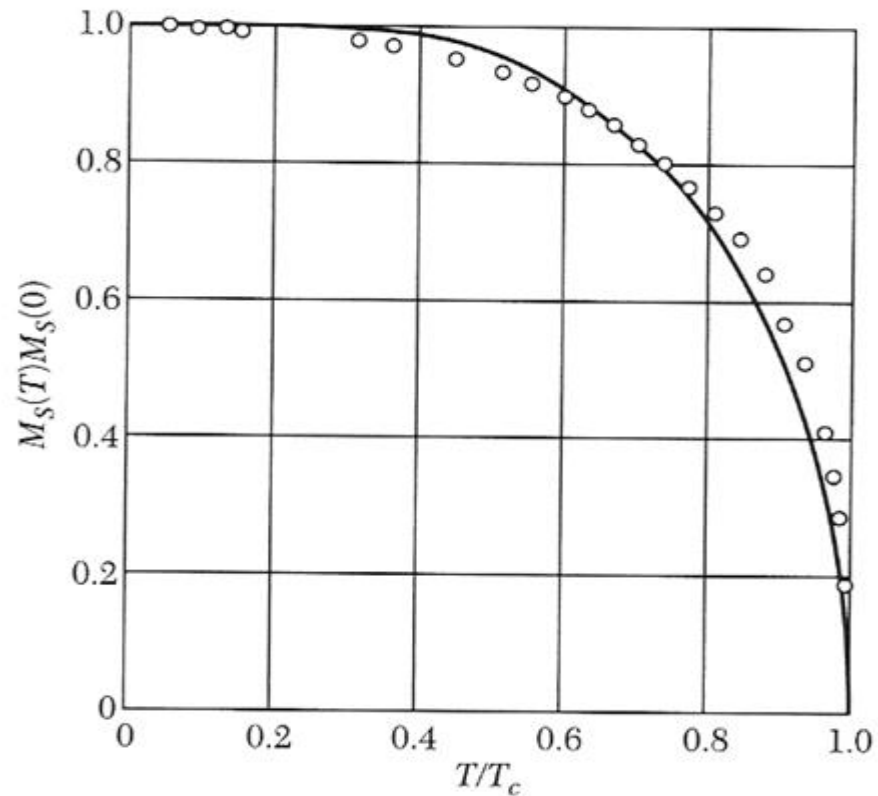
minimize m

$$\frac{df}{dm} = 0 = 2\alpha_0 (T - T_c) m + 2\beta m^3$$

The temperature dependence of the magnetization is

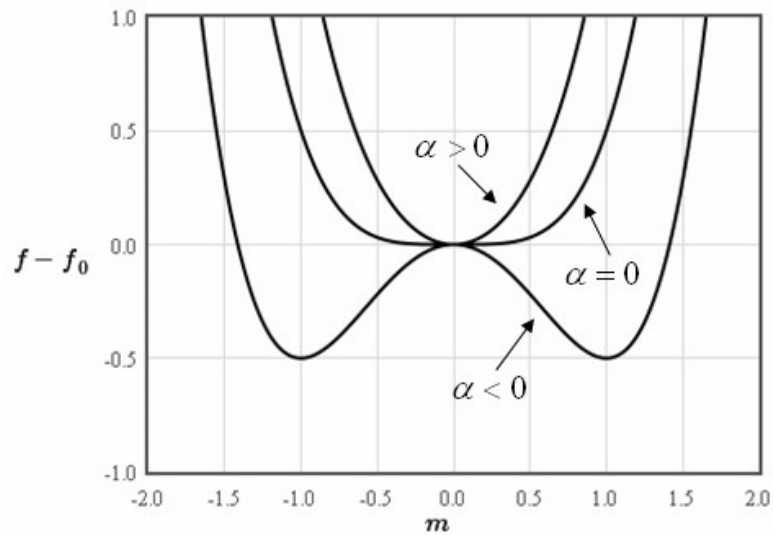
$$m = \pm \sqrt{\frac{\alpha_0 (T_c - T)}{\beta}} \quad T < T_c$$

Landau theory of phase transitions



$$m = \sqrt{\frac{\alpha_0 (T_c - T)}{\beta}} \quad T < T_c$$

Free energy

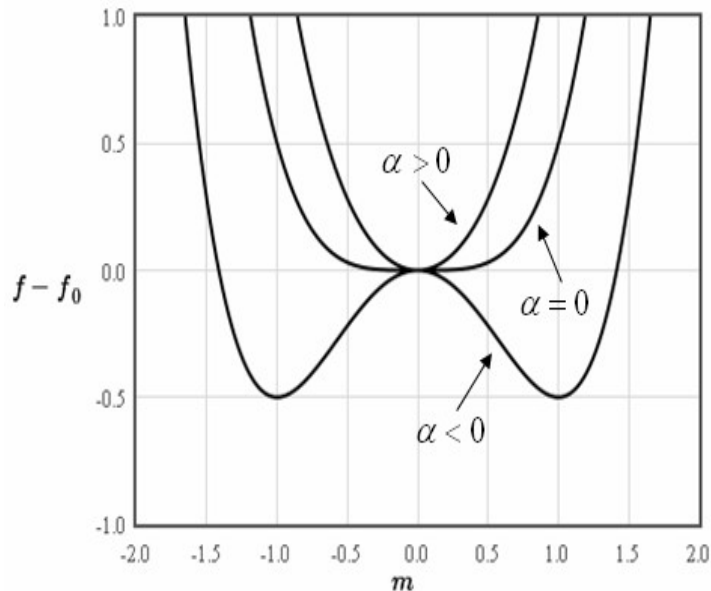


$$f = f_0 + \alpha_0 (T - T_c) m^2 + \frac{1}{2} \beta m^4 + \dots$$

$$m = \pm \sqrt{\frac{\alpha_0 (T_c - T)}{\beta}} \quad T < T_c$$

$$f = f_0 - \frac{\alpha_0^2 (T - T_c)^2}{\beta} + \dots$$

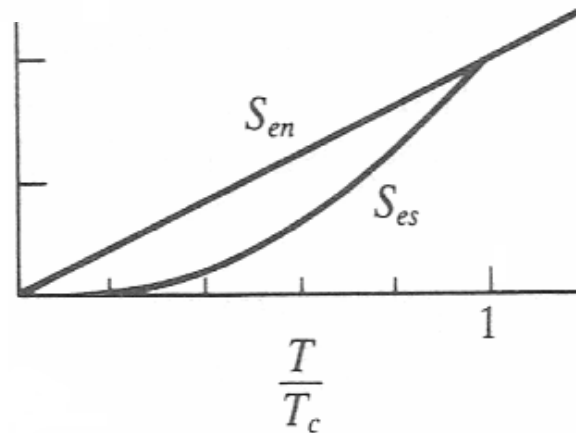
Entropy



$$f = f_0(T) - \frac{\alpha_0^2 (T - T_c)^2}{\beta} + \dots$$

$$s = -\frac{\partial f}{\partial T} = s_0(T) + \frac{2\alpha_0^2 (T - T_c)}{\beta} + \dots$$

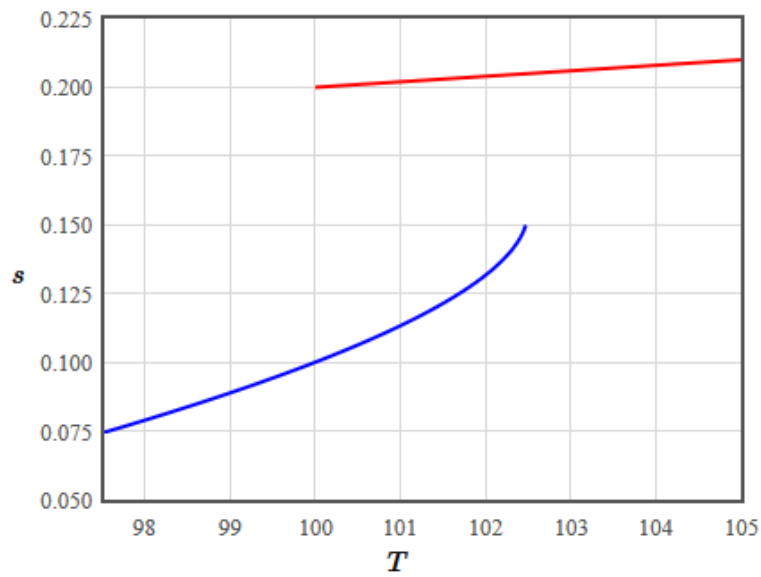
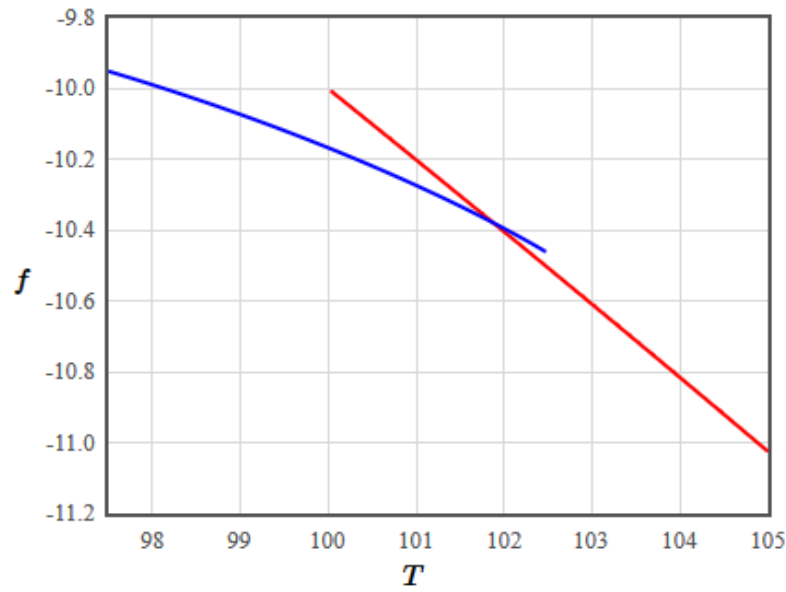
Kink in the entropy



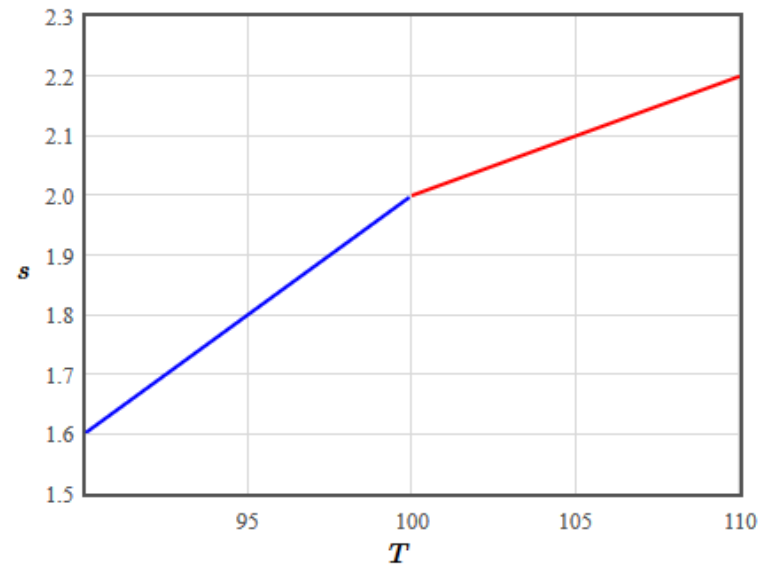
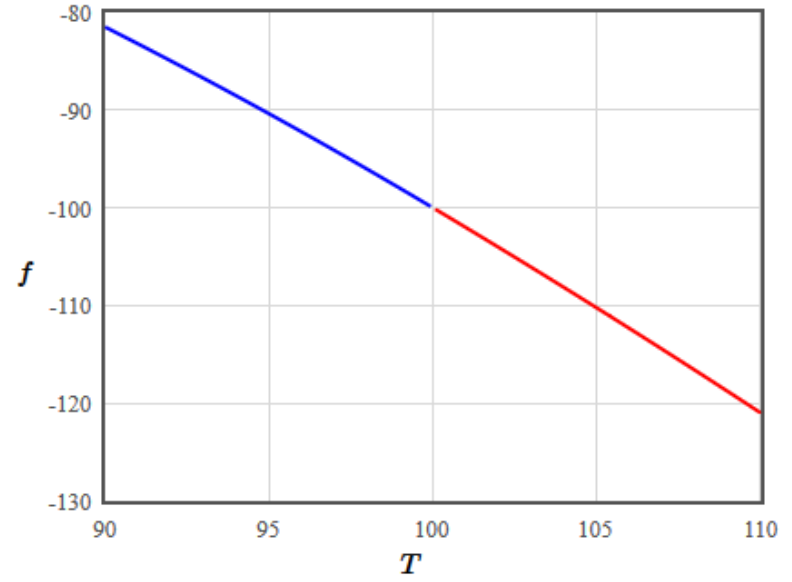
$$L = T_c (S_A - S_B) = 0$$

This is a second order phase transition

1st order



2nd order



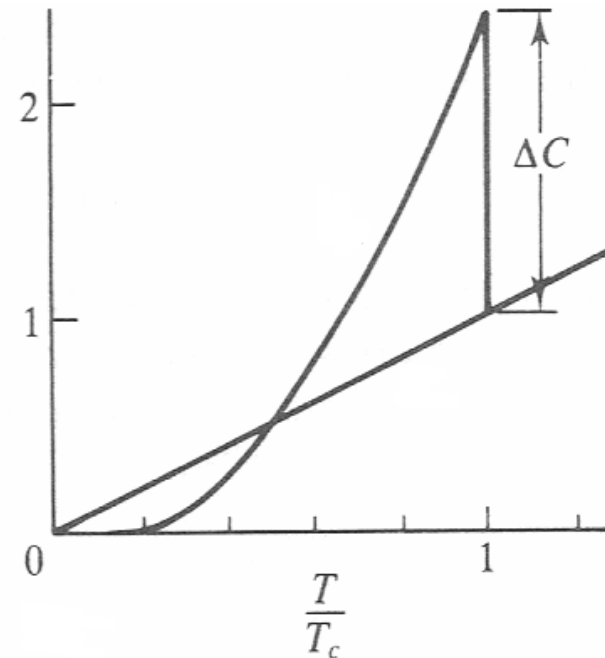
Specific heat

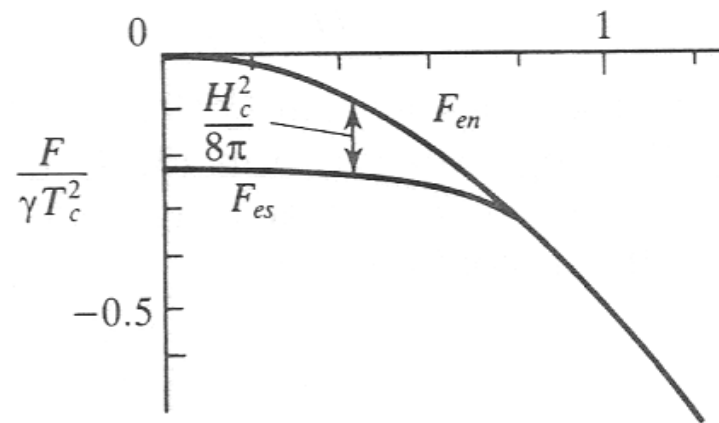
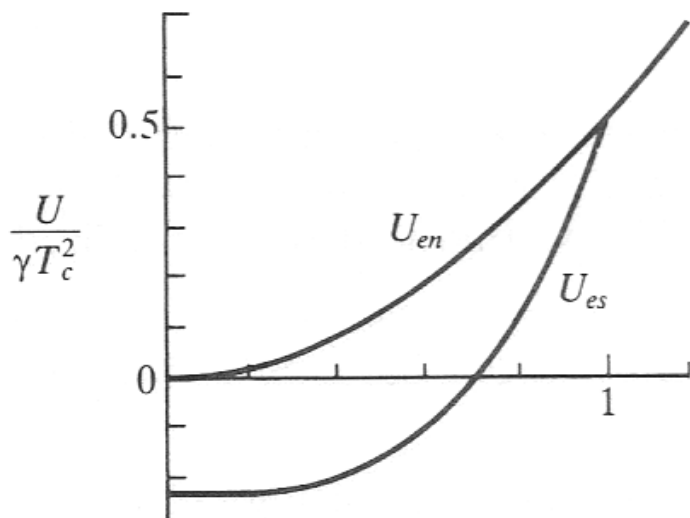
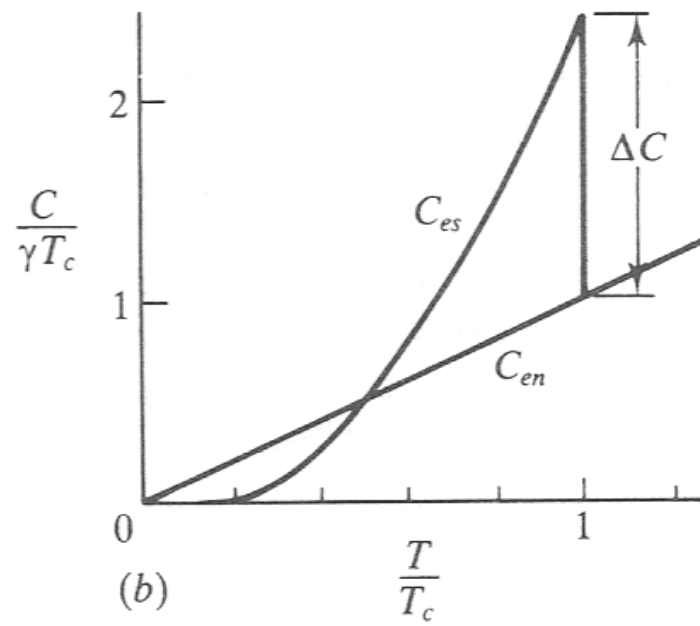
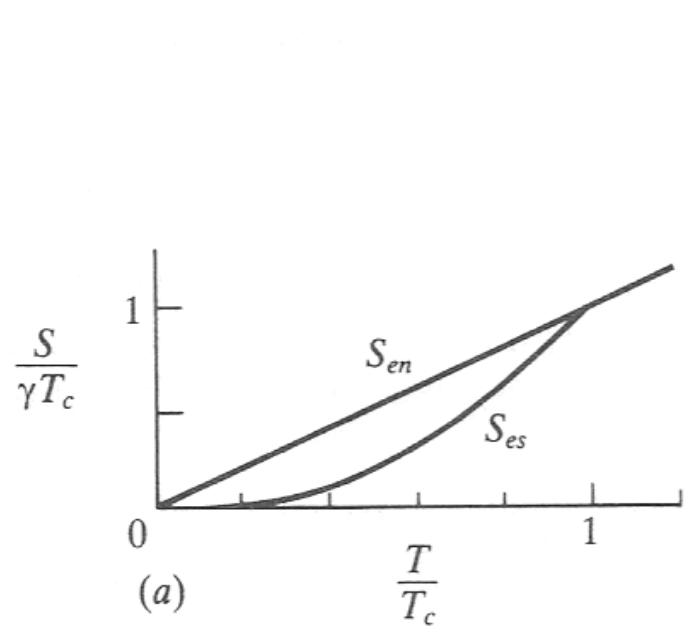
Entropy $s = -\frac{\partial f}{\partial T} = s_0(T) + \frac{2\alpha_0^2(T - T_c)}{\beta} + \dots$

Specific heat $c_v = T \frac{\partial s}{\partial T} = c_0(T) + \frac{2\alpha_0^2 T}{\beta} + \dots \quad T < T_c$

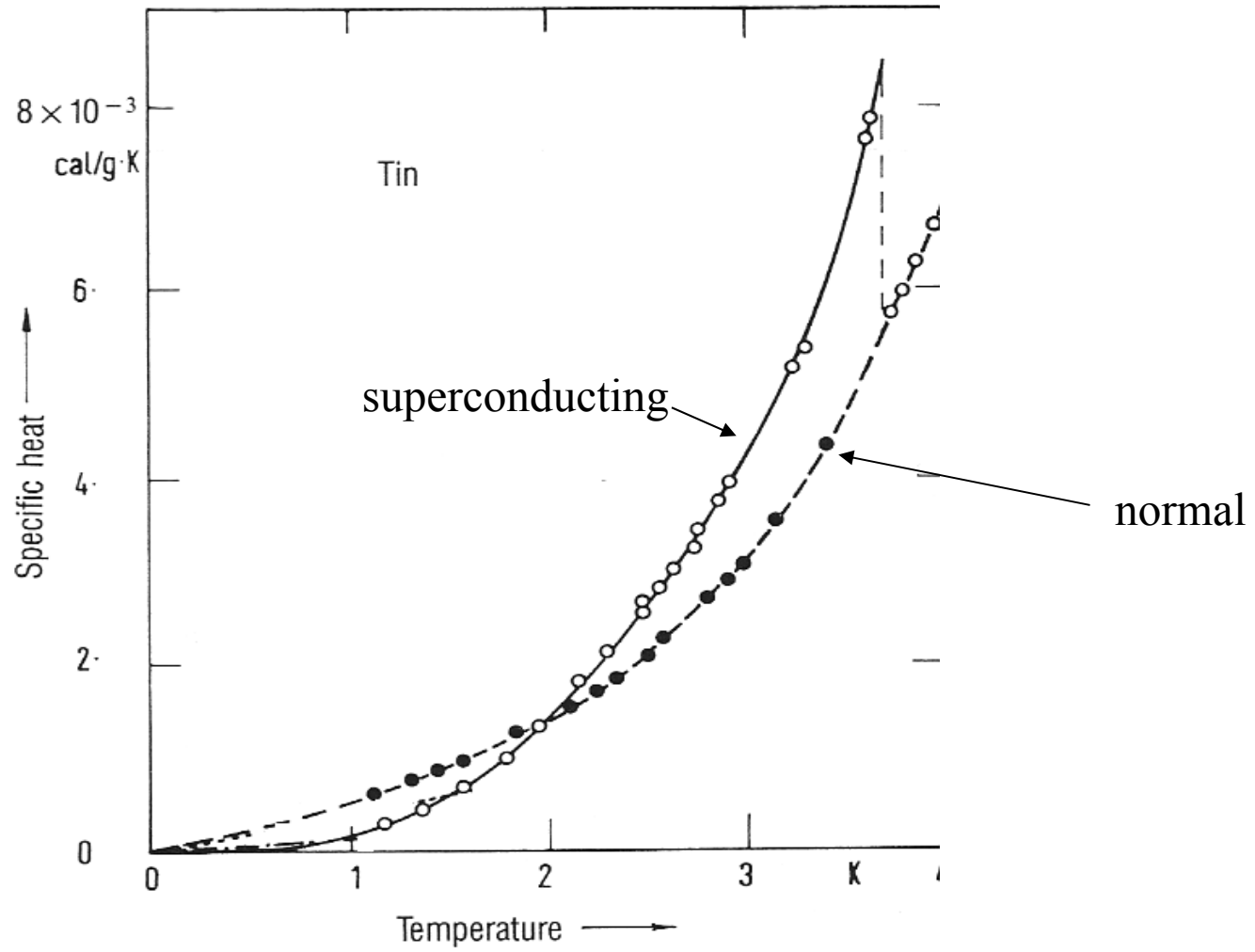
There is a jump in the specific heat at the phase transition and then a linear dependence after the jump.

$$\Delta c_v = \frac{2\alpha_0^2 T_c}{\beta}$$

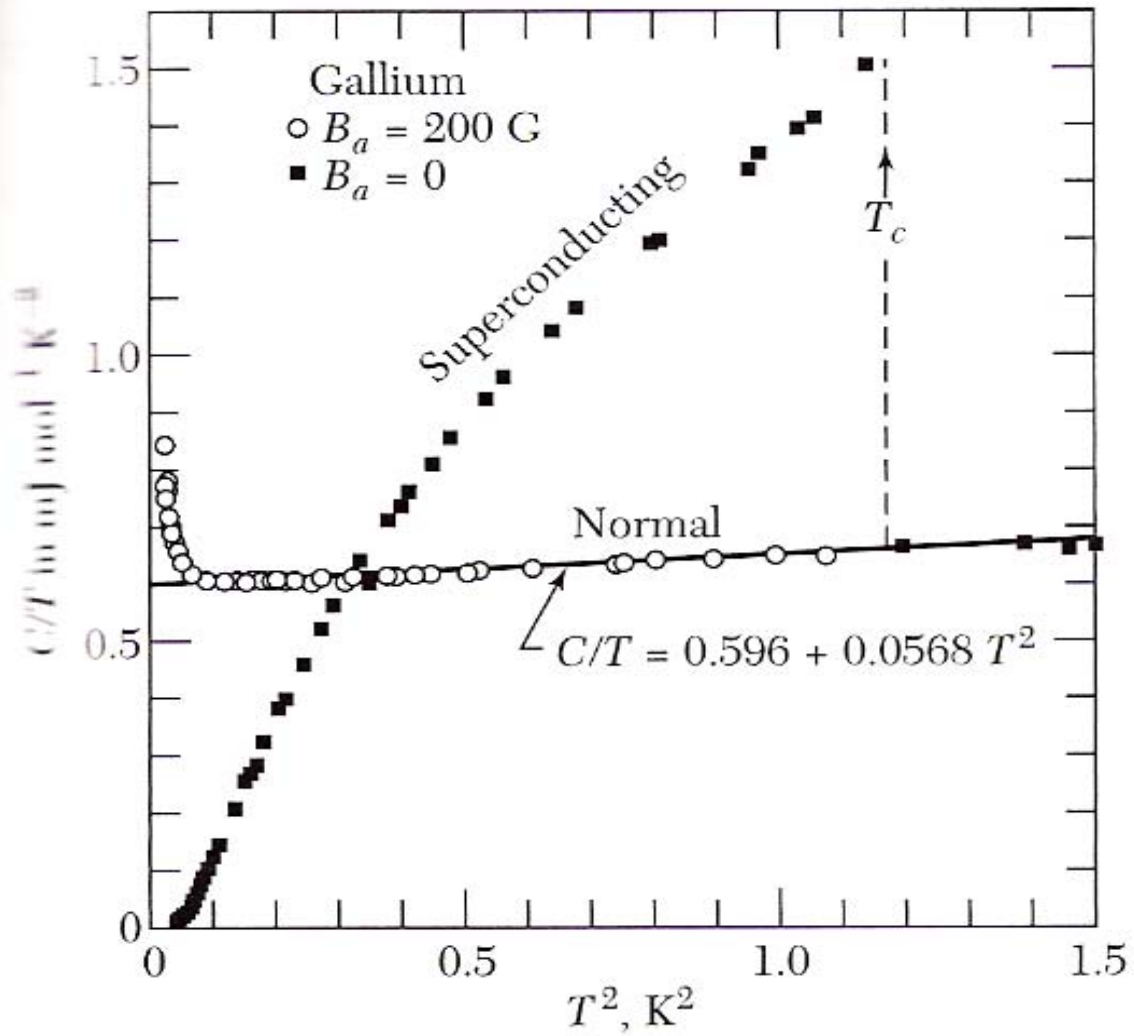




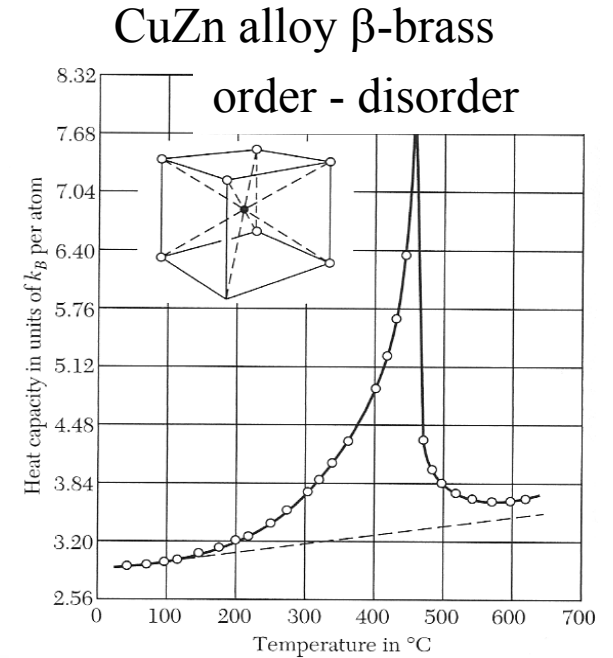
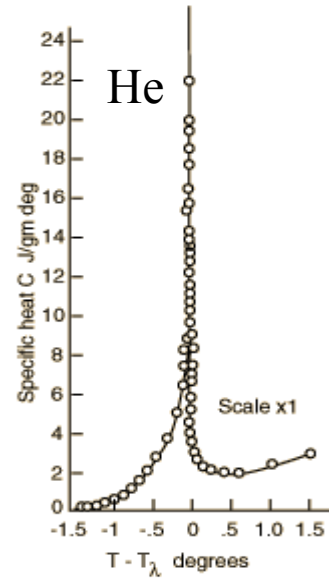
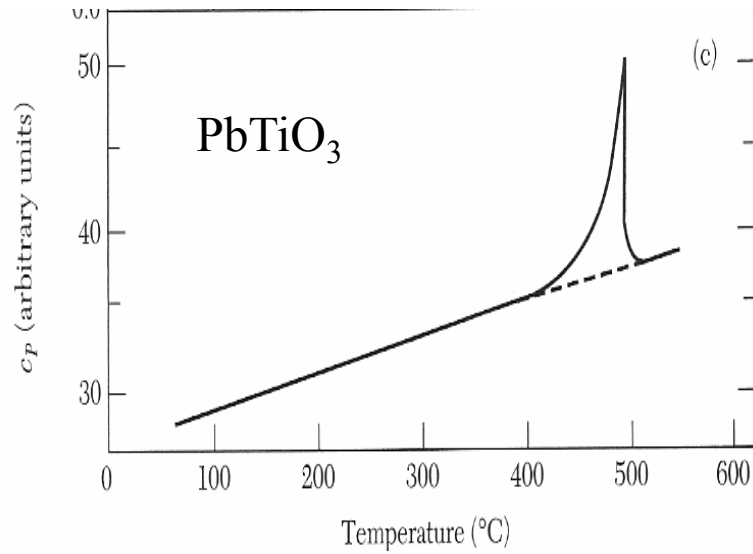
Specific heat



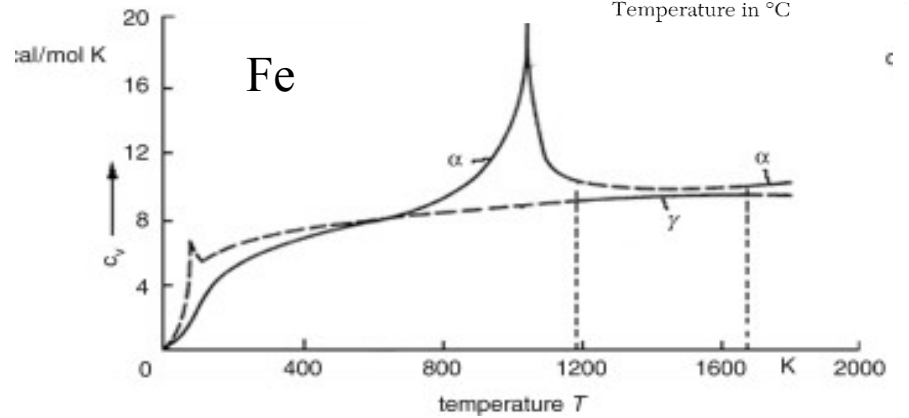
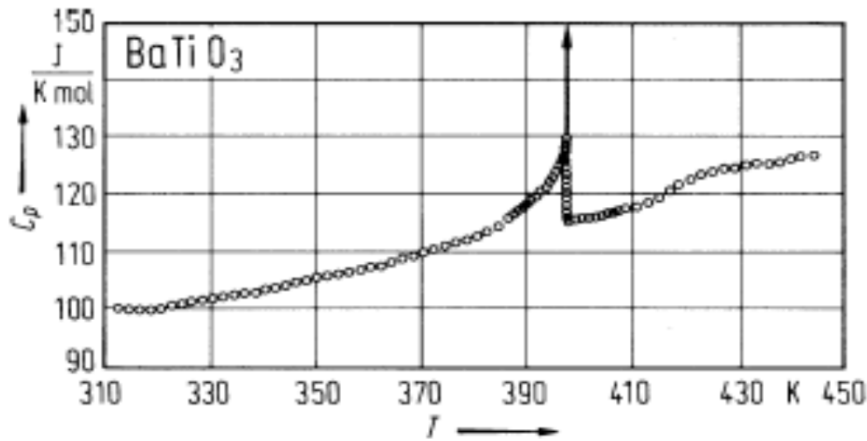
Specific heat



Specific heat



BaTiO₃. Heat capacity vs. temperature [76H].

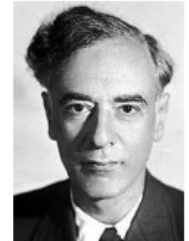


Landau theory of second order phase transitions

Outline
Quantization
Photons
Electrons
Magnetic effects and Fermi surfaces
Linear response
Transport
Crystal Physics
Electron-electron interactions
Quasiparticles
Structural phase transitions
Landau theory of second order phase transitions
Superconductivity
Exam questions
Appendices
Lectures
Books
Course notes
TUG students
Making presentations

Normally, to calculate thermodynamic properties like the free energy, the entropy, or the specific heat, it is necessary to determine the microscopic states of system by solving the Schrödinger equation. For crystals, the microscopic states are labeled by k and the solutions of the Schrödinger equation are typically expressed as a dispersion relation where the energy is given for each k . The dispersion relation can be used to calculate the density of states and the density of states can be used to calculate the thermodynamic properties. This is typically a long and numerically intensive calculation.

Landau realized that near a phase transition an approximate form for the free energy can be constructed without first calculating the microscopic states. He recognized it is always possible to identify an order parameter that is zero on the high temperature side of the phase transition and nonzero on the low temperature side of the phase transition. For instance, the magnetization can be considered the order parameter at a ferromagnetic - paramagnetic phase transition. For a structural phase transition from a cubic phase to a tetragonal phase, the order parameter can be taken to be $c/a - 1$ where c is the length of the long side of the tetragonal unit cell and a is the length of the short side of the tetragonal unit cell.

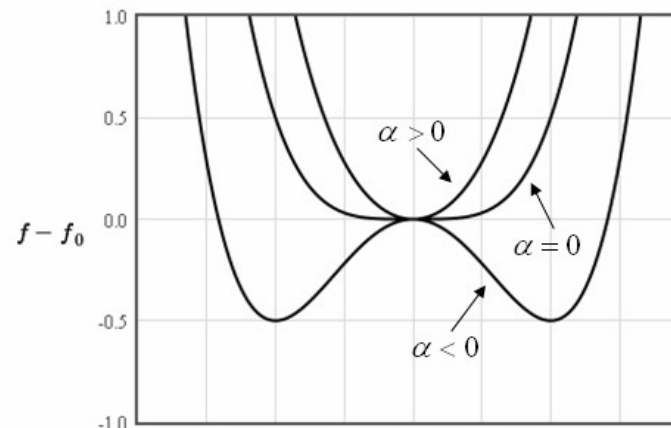


Lev Landau

At a second order phase transition, the order parameter increases continuously from zero starting at the critical temperature of the phase transition. An example of this is the continuous increase of the magnetization at a ferromagnetic - paramagnetic phase transition. Since the order parameter is small near the phase transition, to a good approximation the free energy of the system can be approximated by the first few terms of a Taylor expansion of the free energy in the order parameter.

$$f(T) = f_0(T) + \alpha m^2 + \frac{1}{2} \beta m^4 \quad \alpha_0 > 0, \quad \beta > 0.$$

Here m is the order parameter, α and β are parameters, and $f_0(T)$ describes the temperature dependence of the high temperature phase near the phase transition. It is assumed that $\beta > 0$ so that the free energy has a minimum for finite values of the order parameter. When $\alpha > 0$, there is only one minimum at $m = 0$. When $\alpha < 0$ there are two minima with $m \neq 0$.



Landau theory, susceptibility

Add a magnetic field

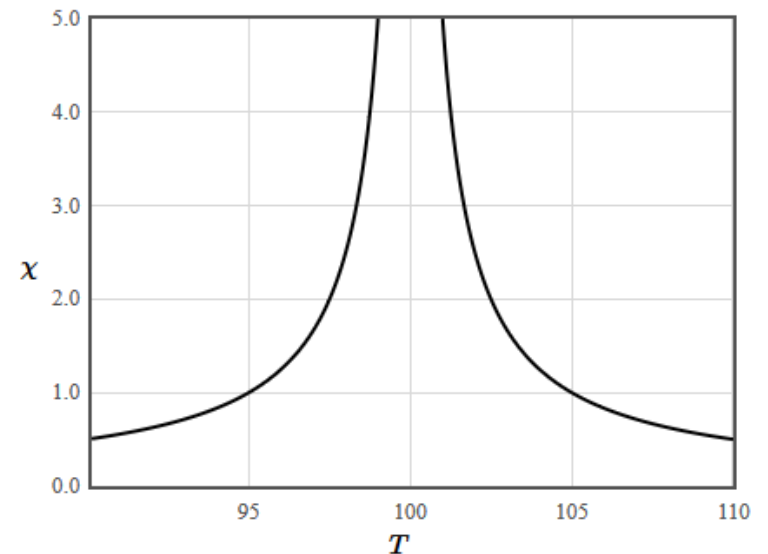
$$f = f_0 + \alpha_0 (T - T_c) m^2 + \frac{1}{2} \beta m^4 - mB$$

$$\frac{df}{dm} = 2\alpha_0 (T - T_c) m + 2\beta m^3 - B = 0$$

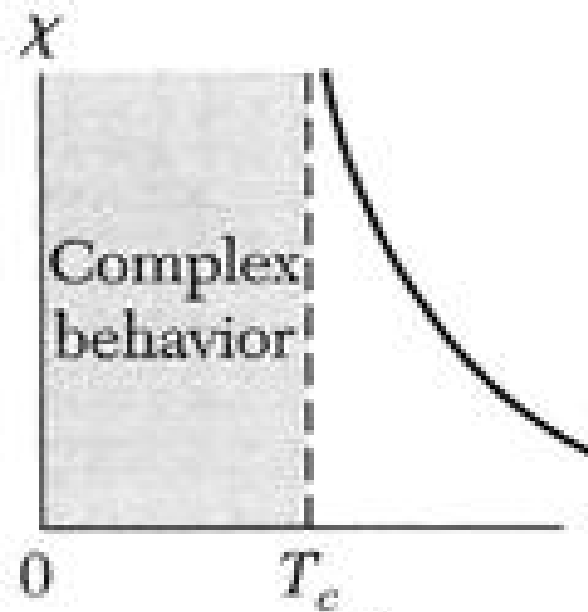
Above T_c , m is finite for finite B . For small m ,

$$m = \frac{B}{2\alpha_0 (T - T_c)} \quad T > T_c$$

$$\chi = \frac{1}{2\alpha_0 (T - T_c)} \quad \text{Curie-Weiss}$$



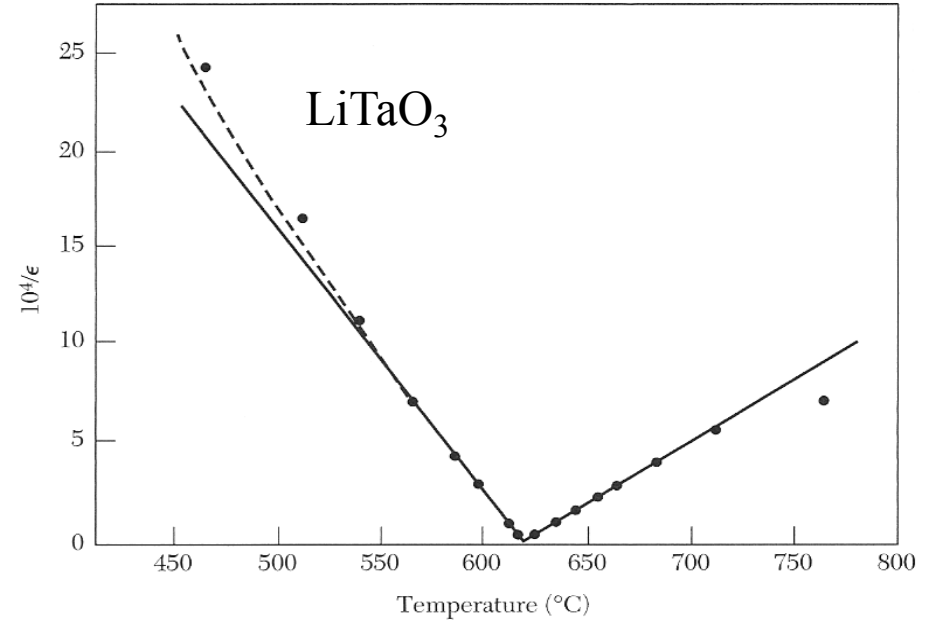
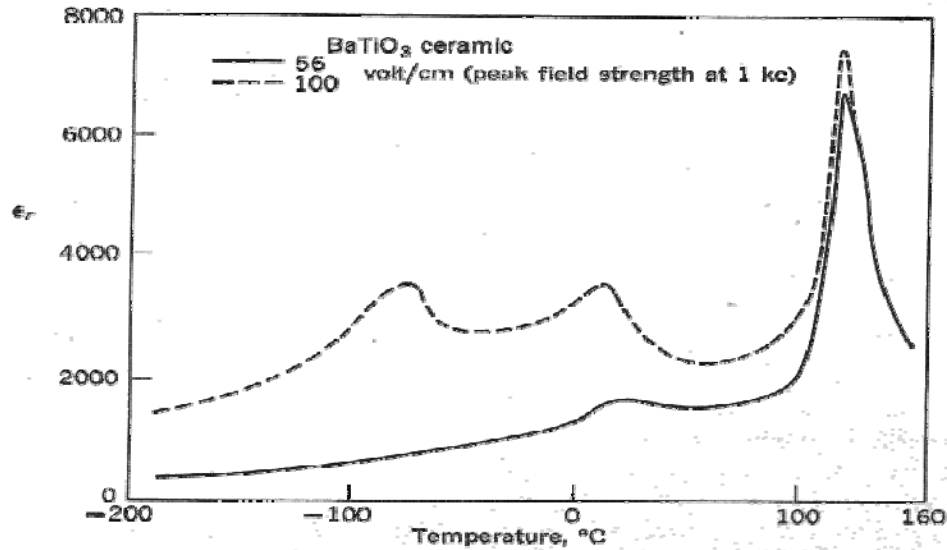
Ferromagnetism



$$\chi = \frac{C}{T - T_c}$$

Curie-Weiss law
($T > T_c$)

Landau theory of phase transitions

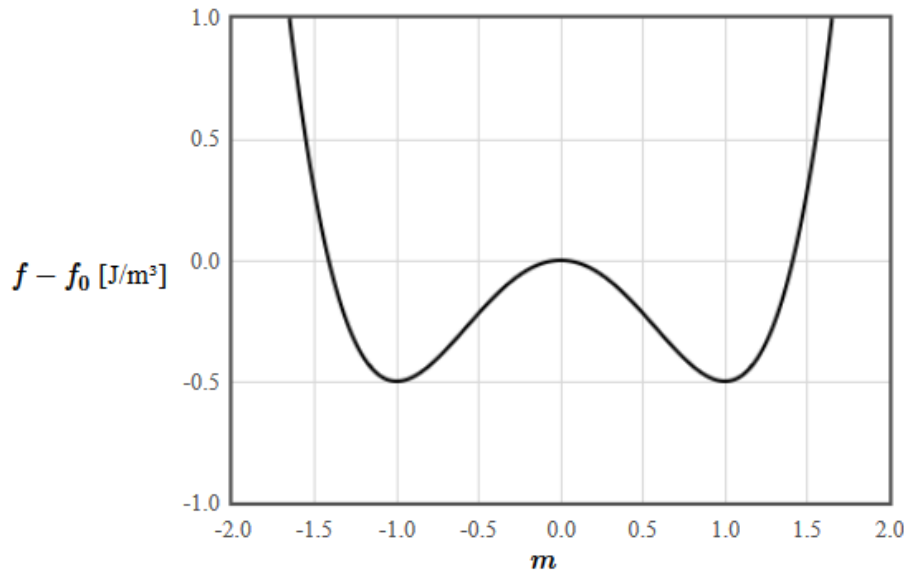


$$\epsilon_r = 1 + \chi$$

$$\chi = \frac{1}{2\alpha_0 (T - T_c)}$$

Curie-Weiss law

Fitting the α_0 and β parameters

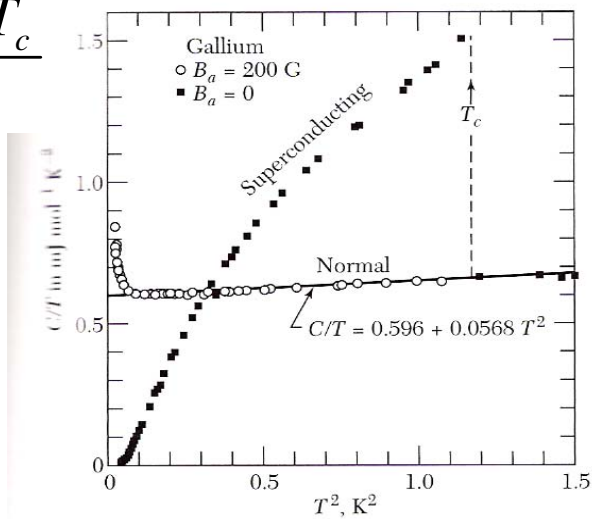


$\alpha_0 =$
 $\beta =$
 $T =$
 $T_c =$
 $f_0(T) =$

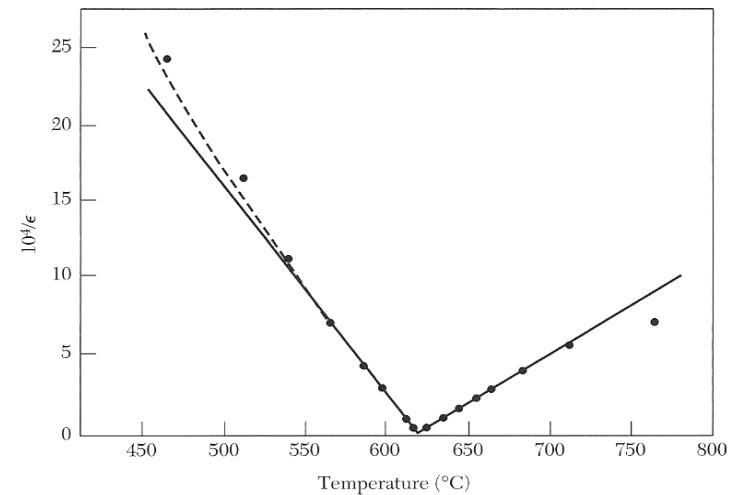
Superconductivity

Ferromagnetism

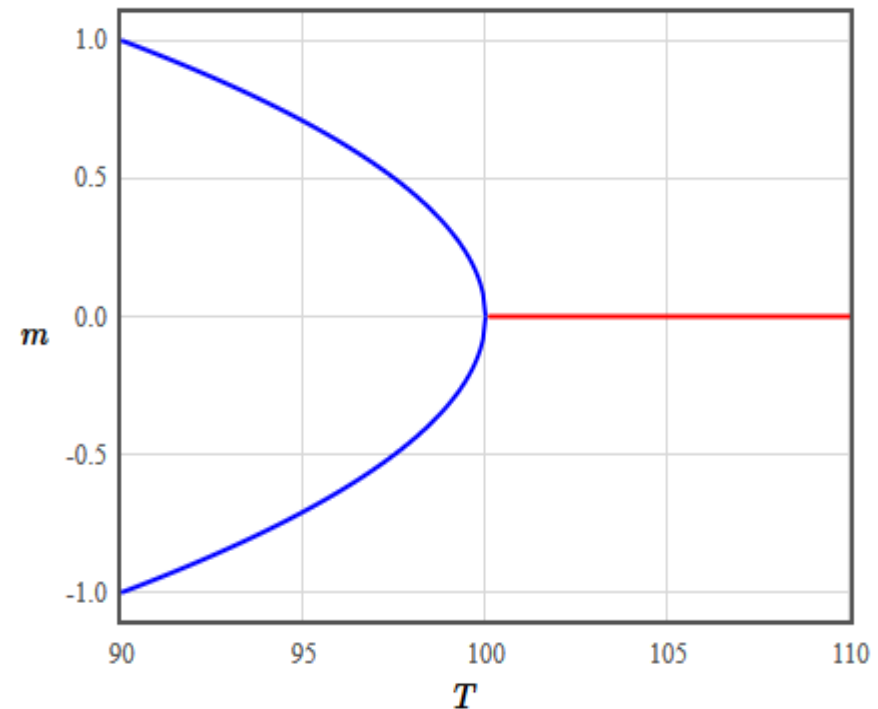
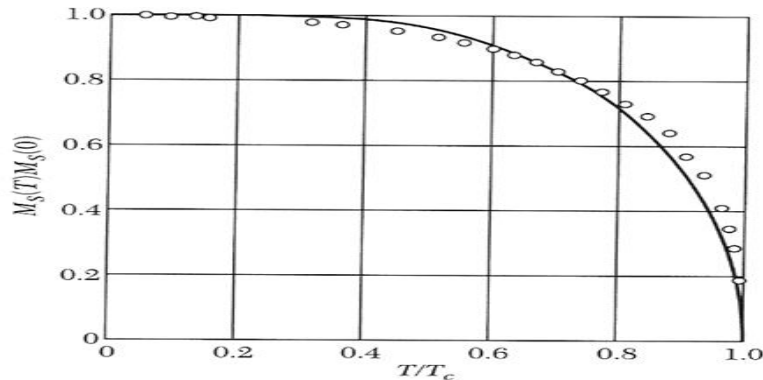
$$\Delta c_v = \frac{2\alpha_0^2 T_c}{\beta}$$



$$\chi = \frac{1}{2\alpha_0 (T - T_c)}$$



Landau theory of phase transitions

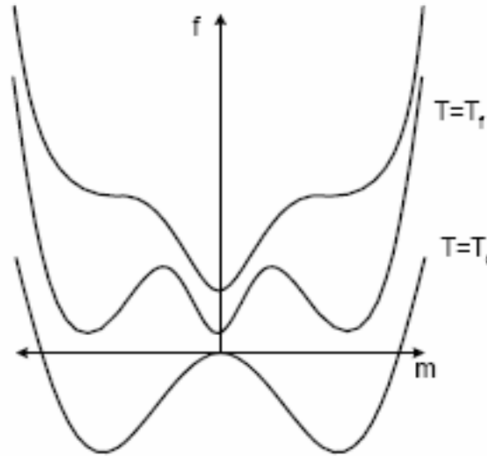


$$m = \sqrt{\frac{\alpha_0 (T_c - T)}{\beta}} \quad T < T_c$$

$\frac{\alpha_0}{\beta}$ can be determined from the temperature dependence of the order parameter

First order transitions

$$f = f_0 + \alpha_0 (T - T_c) m^2 + \frac{1}{2} \beta m^4 + \frac{1}{3} \gamma m^6 + \dots \quad \alpha_0 > 0, \quad \beta < 0, \quad \gamma > 0$$



There is a jump in the order parameter at the phase transition.