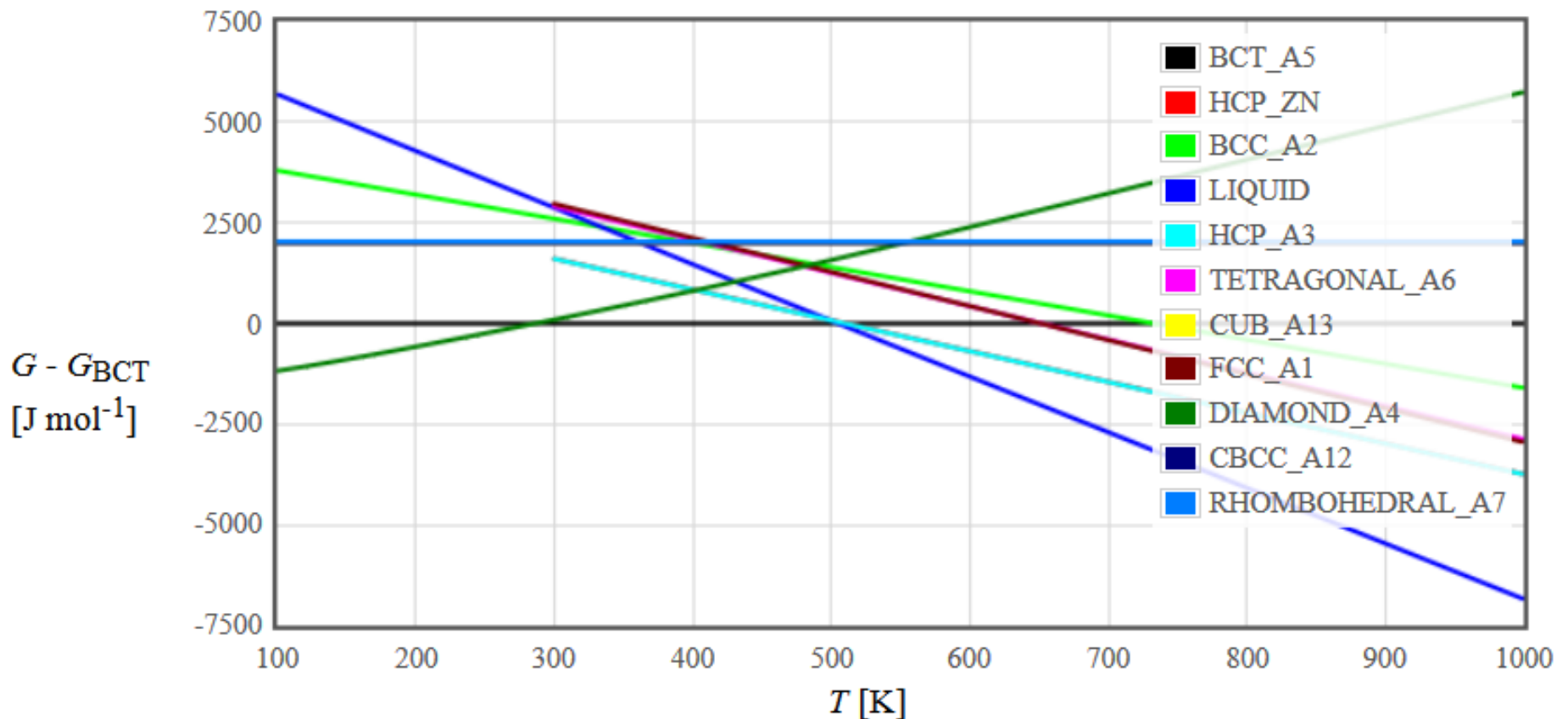


24. Phase Transitions

Jan. 14, 2018

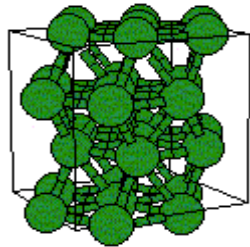
Structural phase transition in Sn

metal β Sn = A5



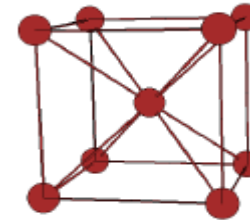
<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

Structural phase transitions

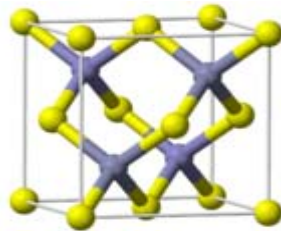


α -Ti, hcp

transition at 890 C



β -Ti, bcc



Zincblende, ZnS

transition at 1020 C



Wurtzite, ZnS

The crystal structure with the lowest free energy will be observed.
Softer phonons >> lower Debye frequency >> more modes occupied >> higher entropy

Ti phonon dispersion

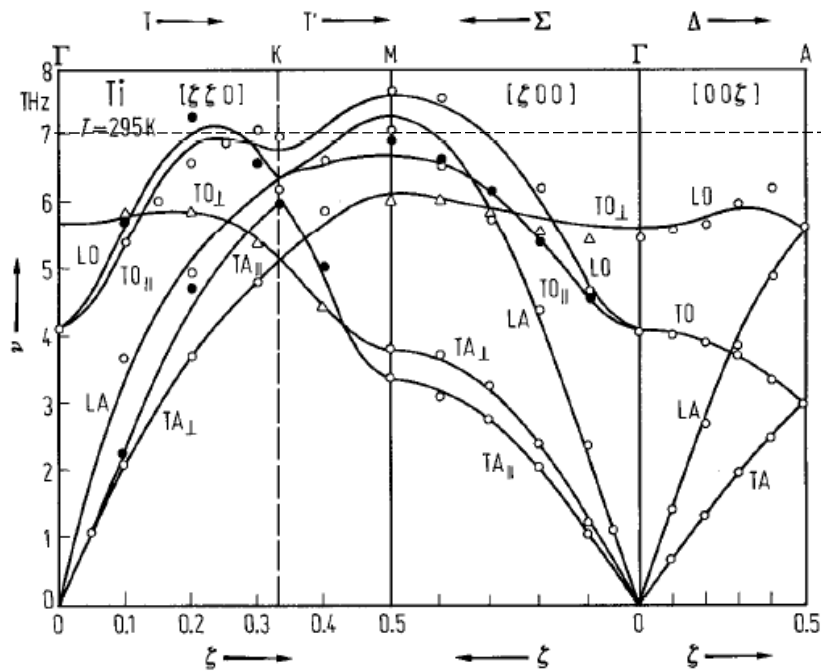


Fig. 1. Ti. Measured phonon dispersion curves at 295 K. The solid lines were obtained from the sixth neighbour Born-von Karman model of Table 3 Ti [79St2].

Springer Materials

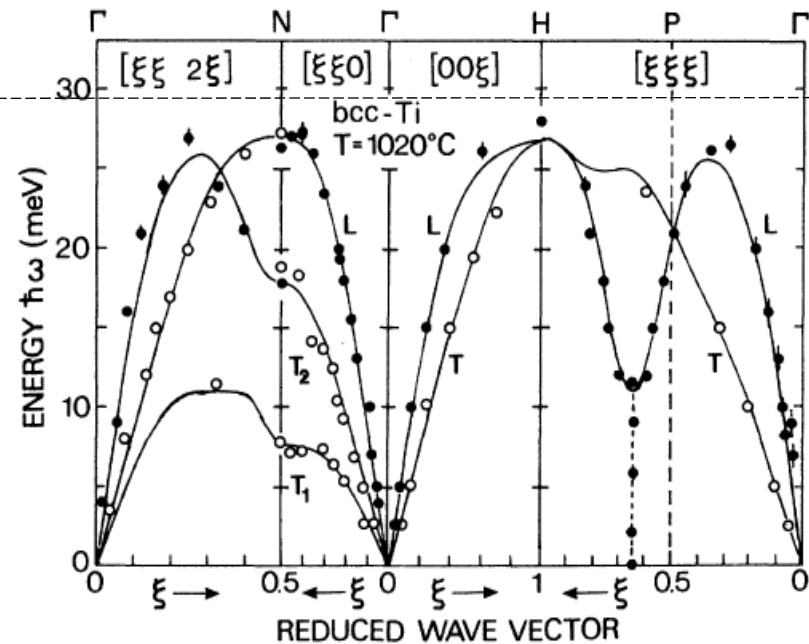


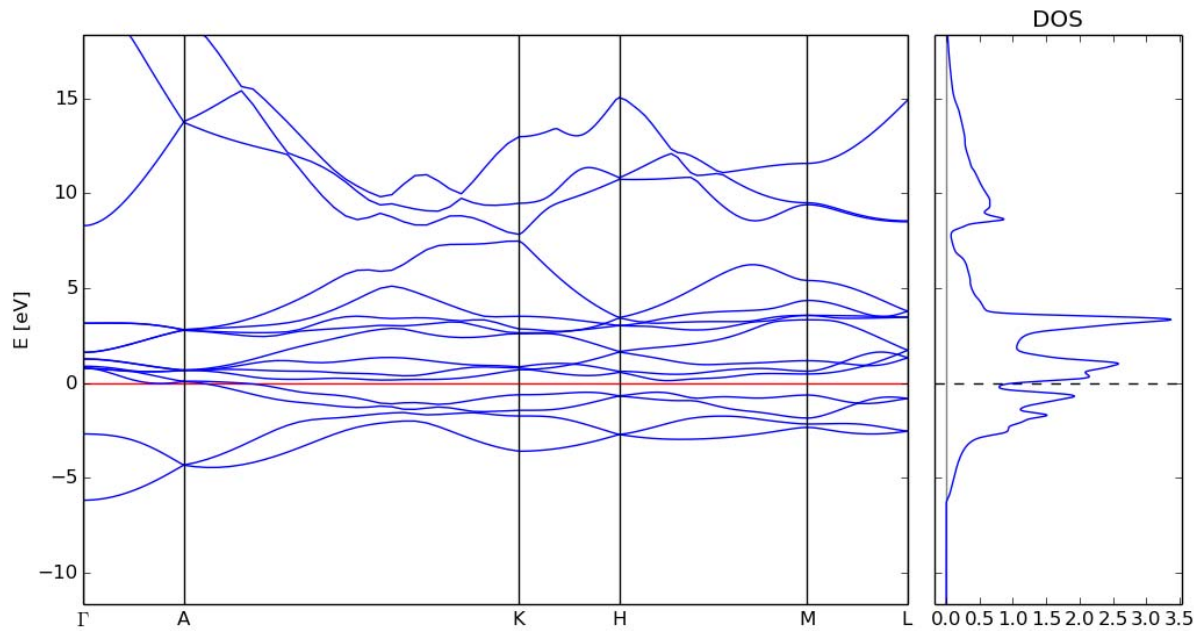
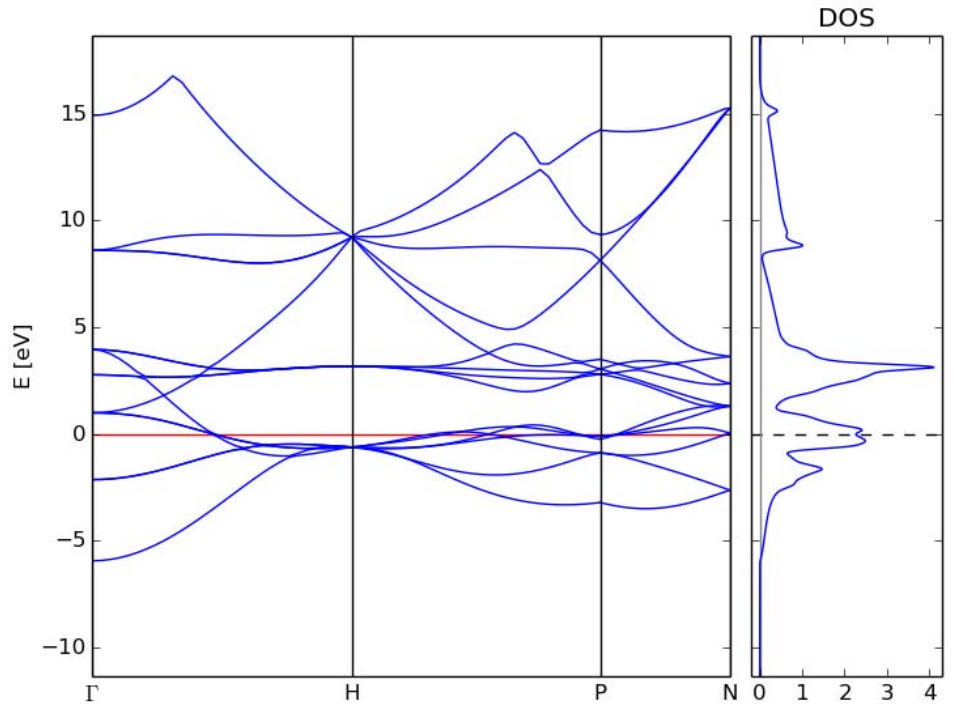
FIG. 2. Phonon dispersion for bcc Ti measured at 1020°C. (The $T_1[\xi\xi 0]$ branch has been measured at 965°C). The solid line shows a Born-von Kármán fit with force constants up to the fifth nearest-neighbor shell.

Phonon dispersion of the bcc phase of group-IV metals. I. bcc titanium, W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, Phys. Rev. B 43, 10933 – (1991)

Titanium



bcc →

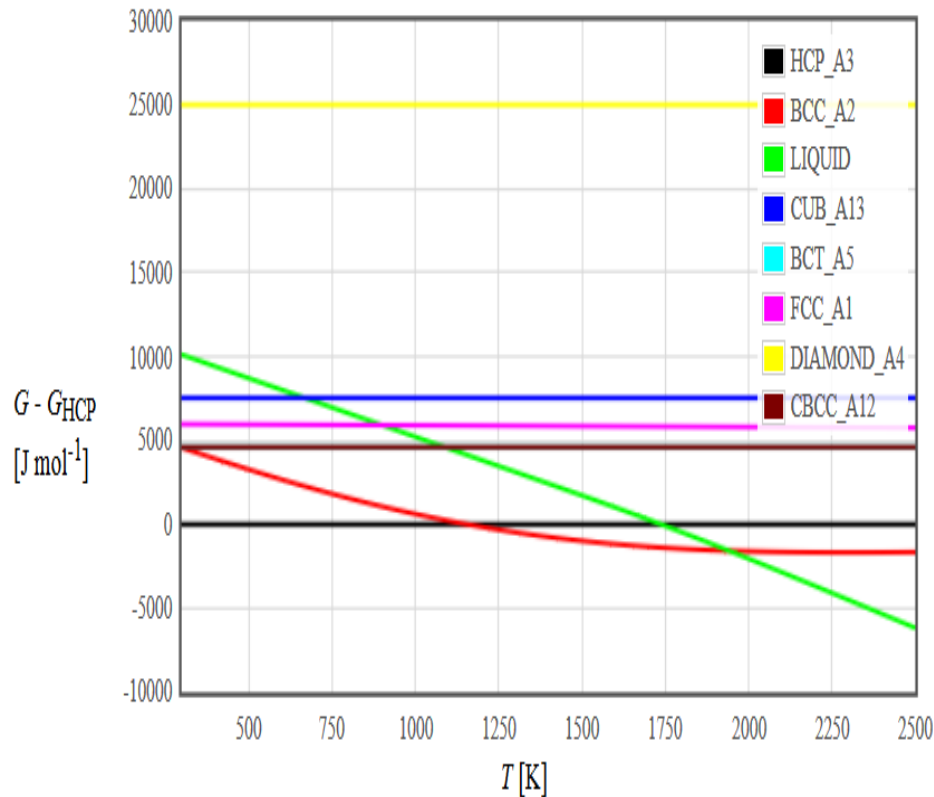


← hcp

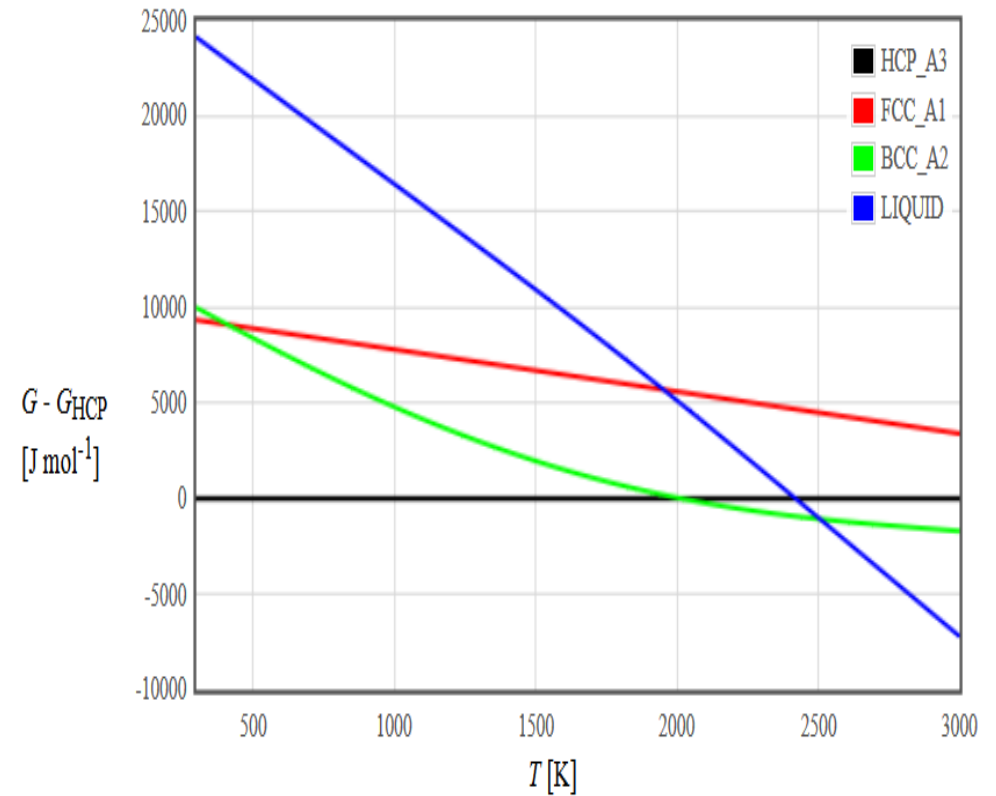
Calculated using FHI-aims by Lydia Nemeč

Close packed \rightarrow bcc

Ti



Hf



Close packed \rightarrow bcc: Am, Be, Ca, Gd, Nd, Pr, Hf, Sc, Sm, Sr, Ti, Tb, Th, Tl, Y, Yb, Zr

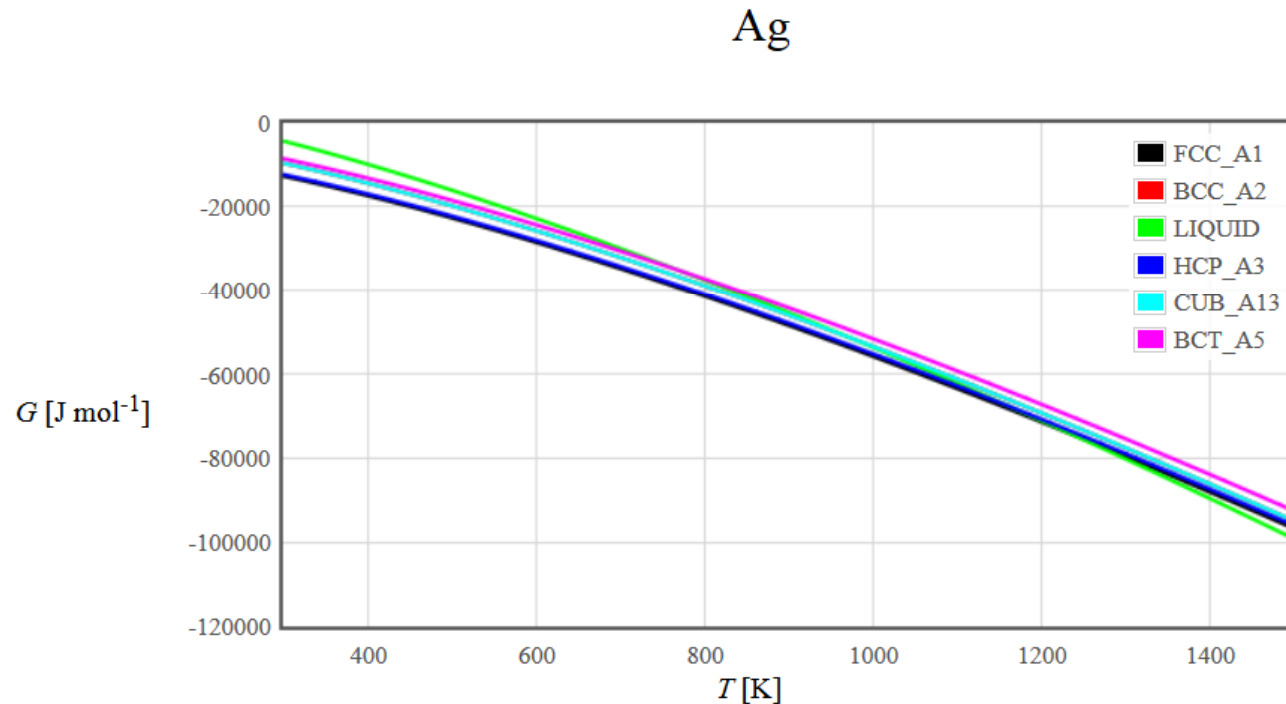
<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

SGTE thermodynamic data

The [Scientific Group Thermodata Europe SGTE](http://www.sgte.org) maintains [thermodynamic databanks for inorganic and metallurgical systems](http://www.sgte.org). Data from their 'pure element database' is plotted below.

Typically, experiments are performed at constant pressure p , temperature T , and number N . Under these conditions, the system will go to the minimum of the Gibbs energy $G = U + pV - TS$. Here U is the internal energy, V is the volume, and S is the entropy. The top plot is the Gibbs energy per mole.

Ag	Al	Am	As
Au	B	Ba	Be
Bi	C	Ca	Cd
Ce	Co	Cr	Cs
Cu	Dy	Er	Eu
Fe	Ga	Gd	Ge
Hf	Hg	Ho	In
Ir	K	La	Li
Lu	Mg	Mn	Mo
N	Na	Nb	Nd
Ni	Np	O	Os
P	Pa	Pb	Pd
Pr	Pt	Pu	Rb
Re	Rh	Ru	S
Sb	Sc	Se	Si
Sm	Sn	Sr	Ta
Tb	Tc	Te	Th
Ti	Tl	Tm	U
V	W	Y	Yb
Zn	Zr		



Since the Gibbs energies of the different phases fall almost on top of each other, it is convenient to plot them relative to the phase that has the lowest Gibbs energy at low temperature.

<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

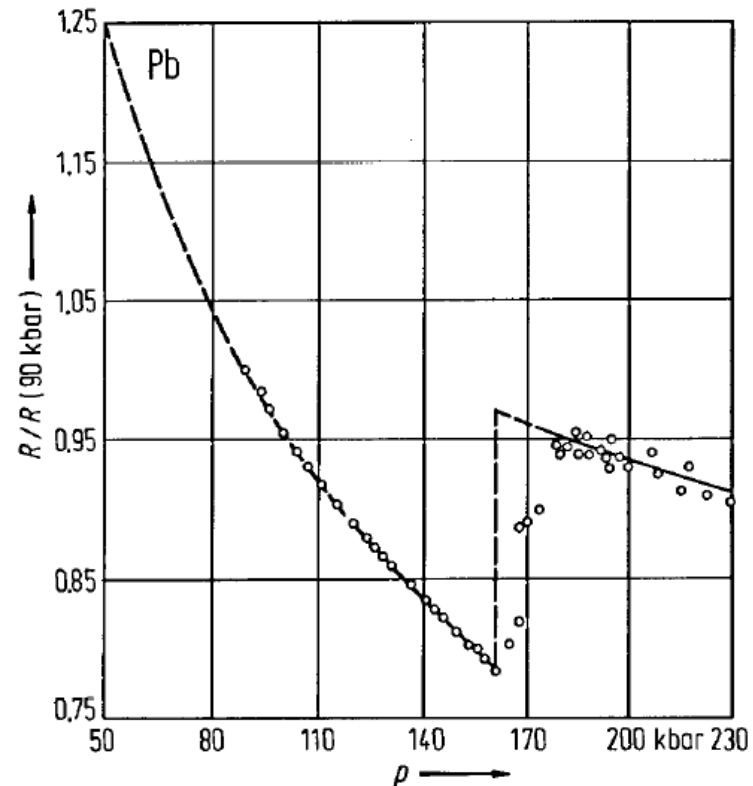
Strain

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

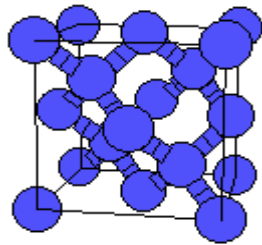
This changes the density of states and the thermodynamic properties.

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.

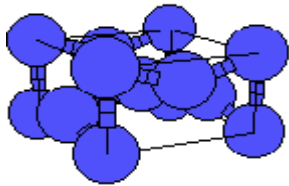


Structural phase transitions in Si



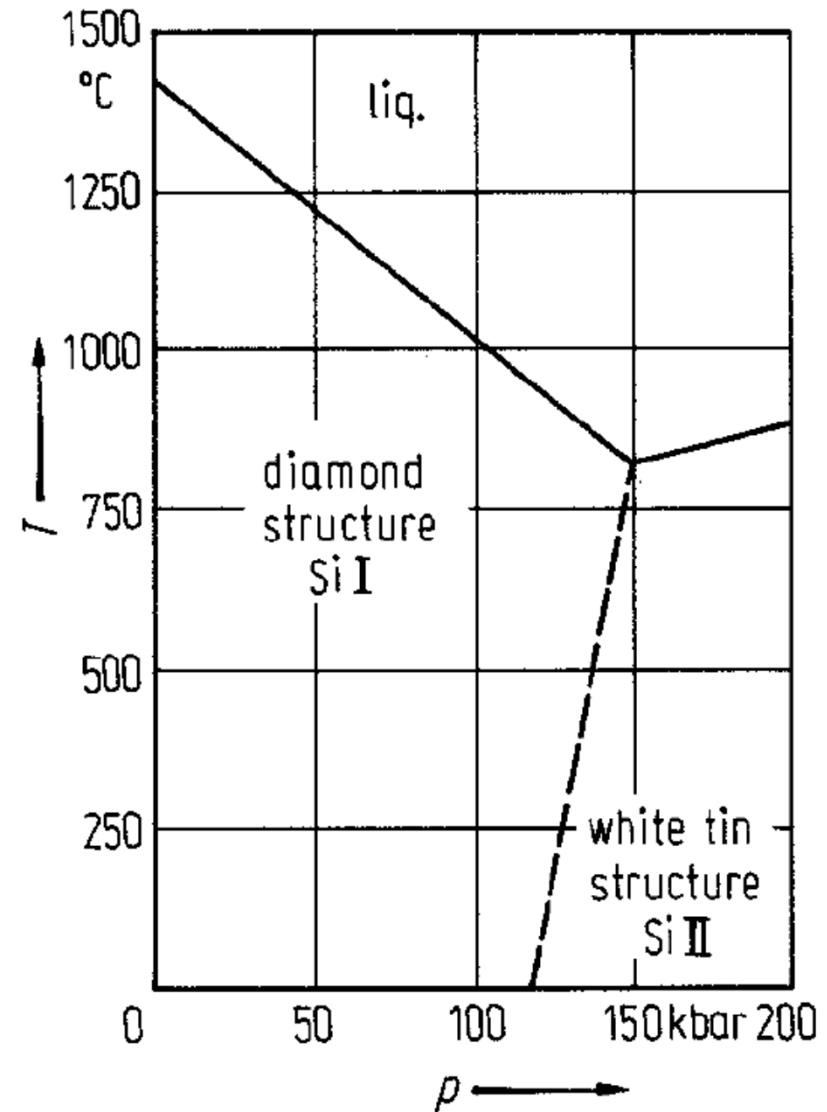
α -Sn, gray tin, diamond

transition at 13 C

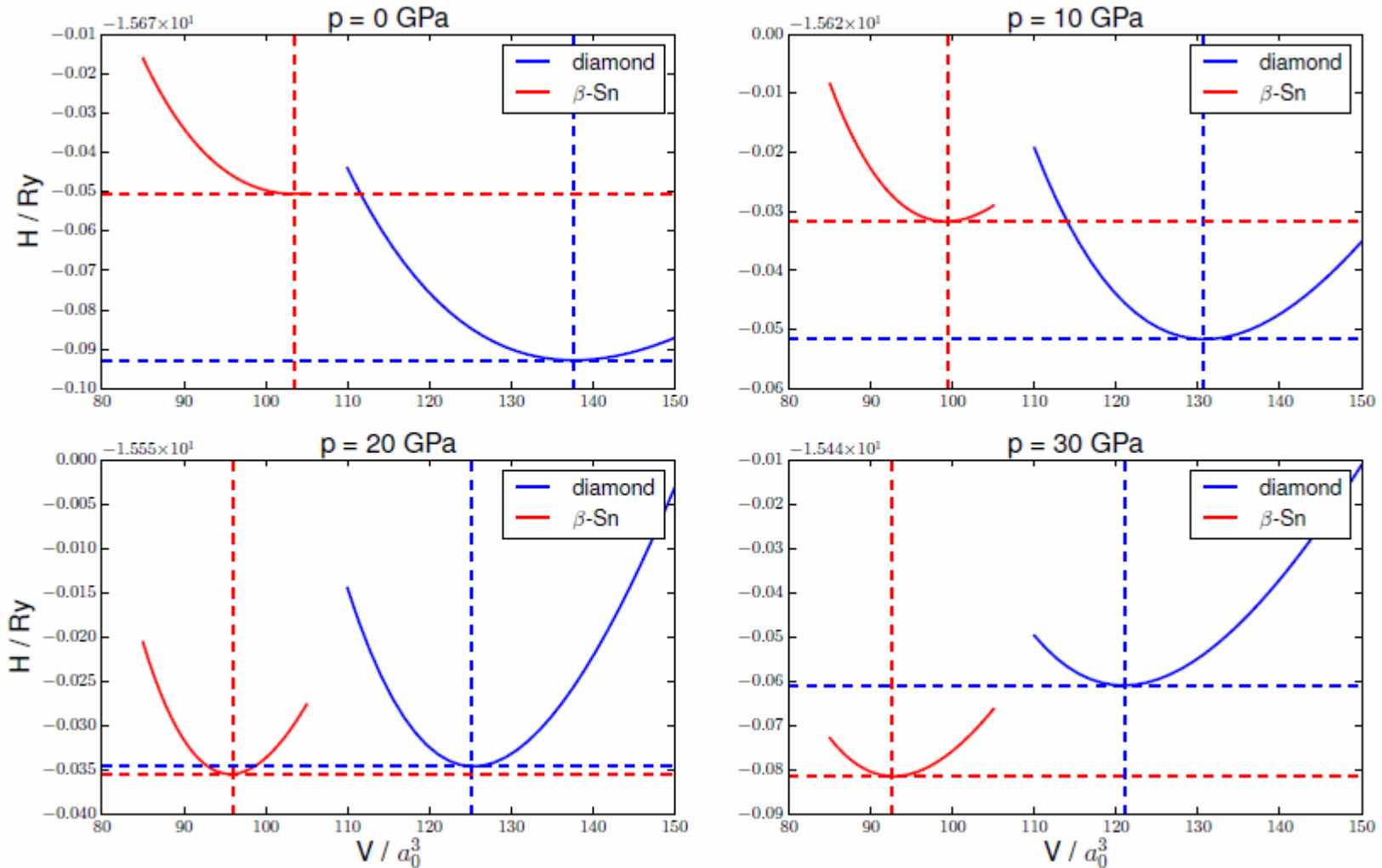


β -Sn, white tin, tetragonal

silicon makes a diamond to β -Sn transition under pressure



Structural phase transition in Si



Structural phase transition in Si

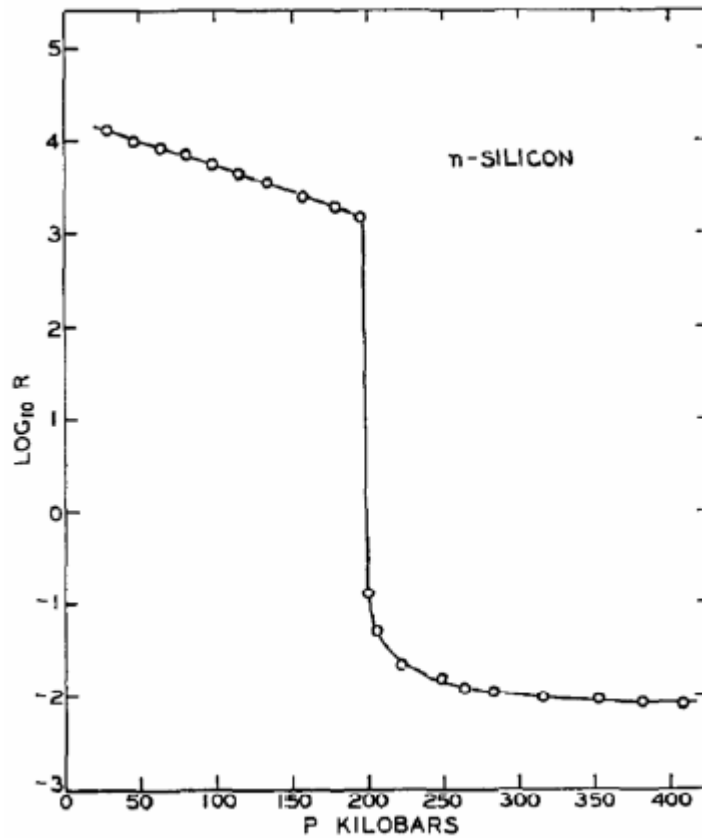
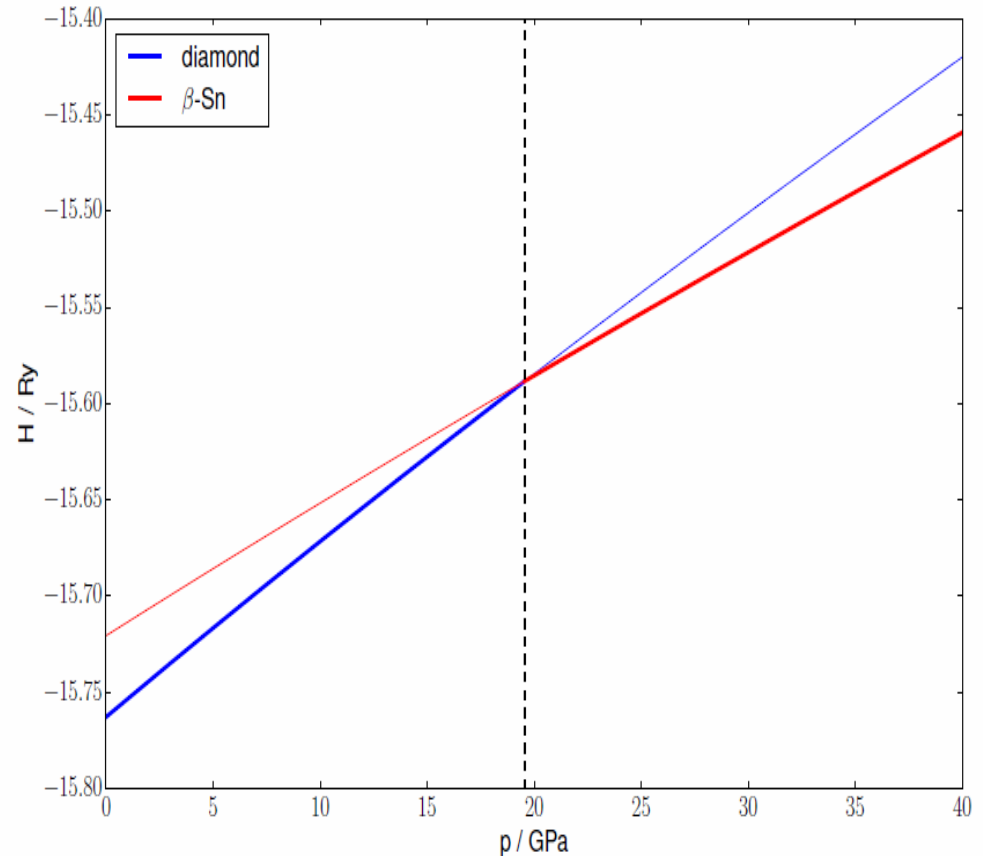


FIG. 1. Resistance vs. pressure—*n*-Silicon.



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

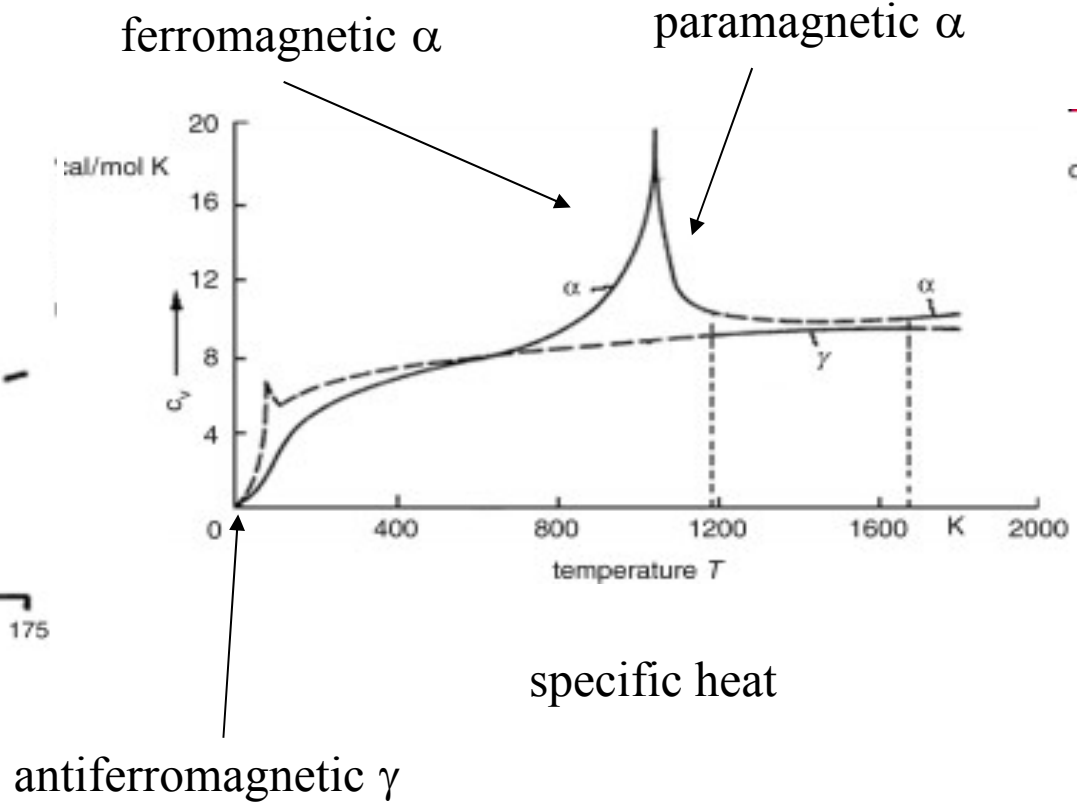
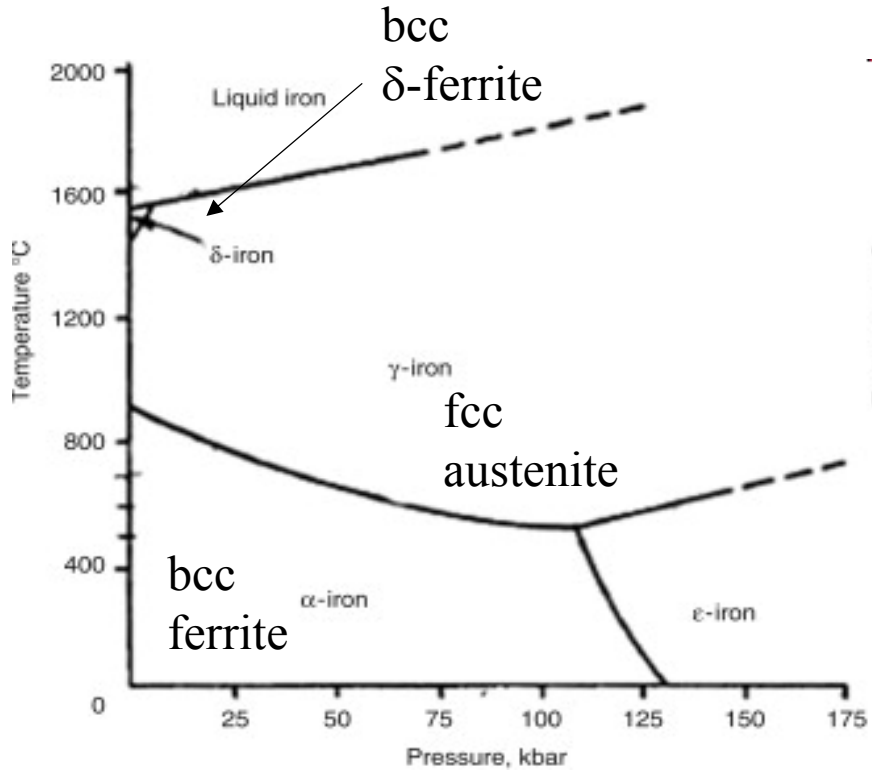
The phase stability of many elements shows the following pattern:

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.

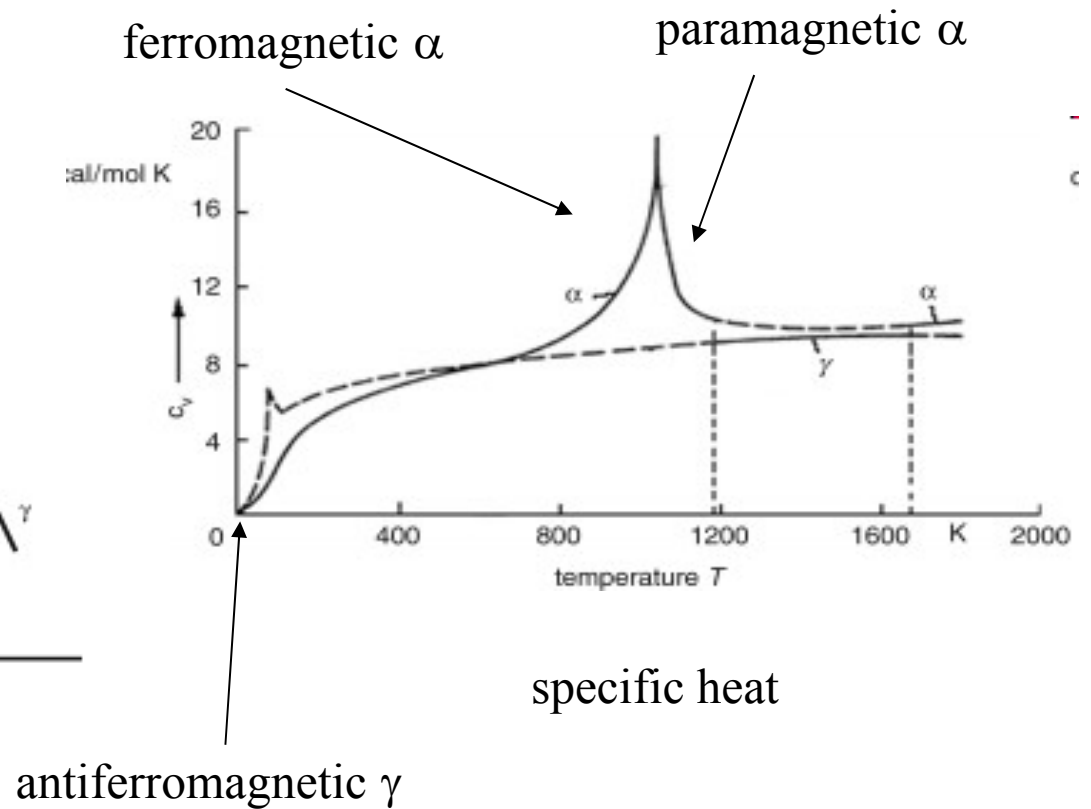
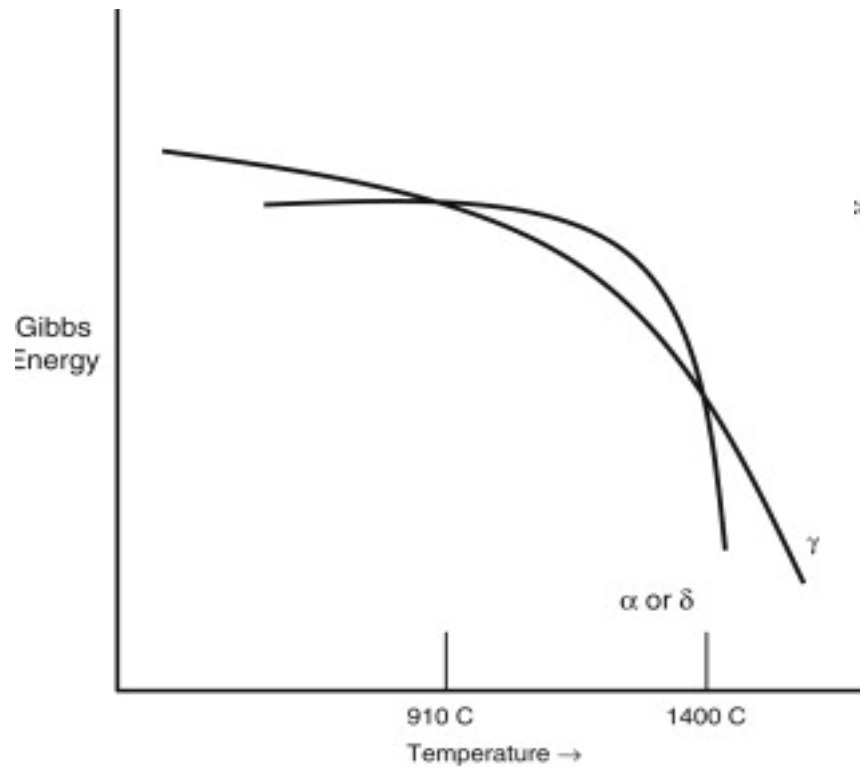
$$G = U + pV - TS$$

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

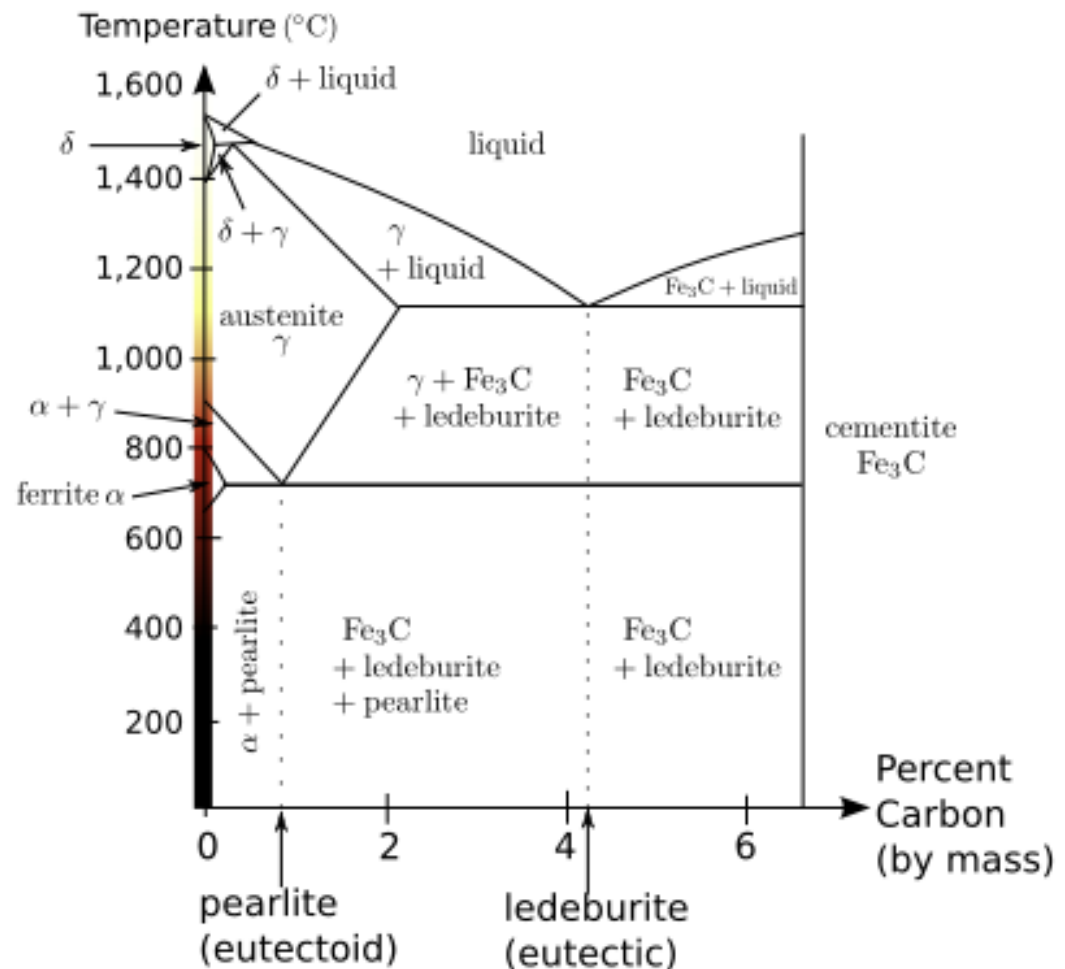
Gray iron

Malleable iron

White iron

Wrought iron (contains slag)

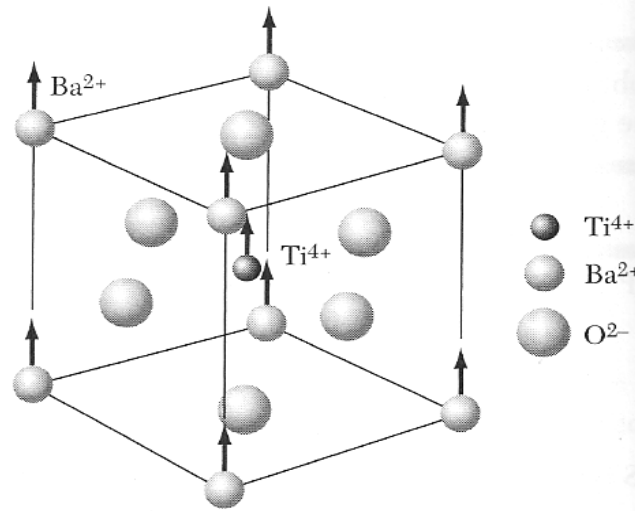
v · d · e



Ferroelectricity

Ferroelectricity

ABX₃
Perovskites

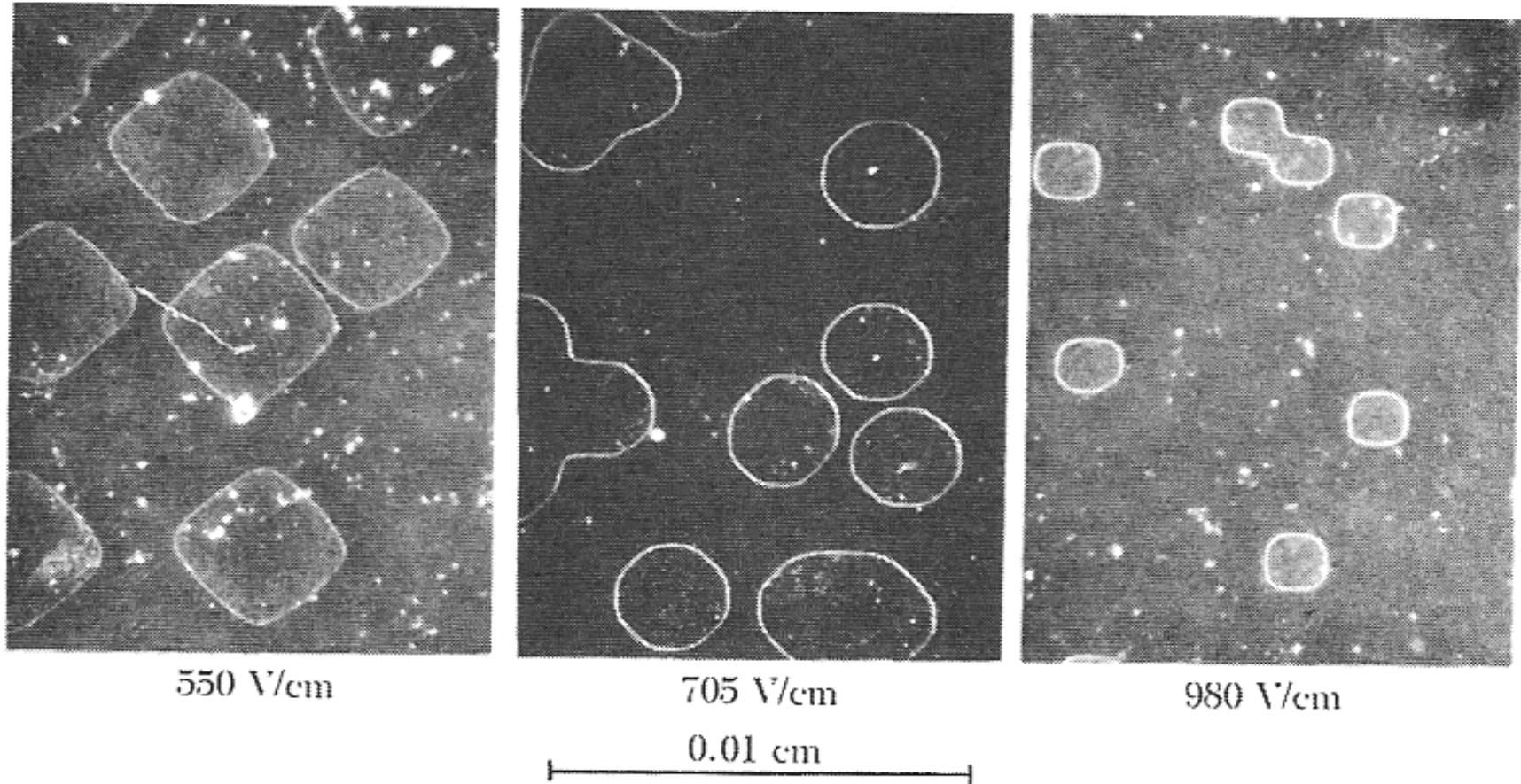


Spontaneous polarization
 Analogous to ferromagnetism
 Structural phase transition
 T_c is transition temperature

Electric field inside the material,
 is not conducting

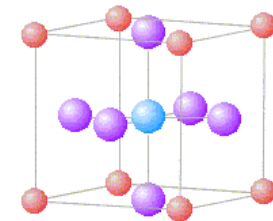
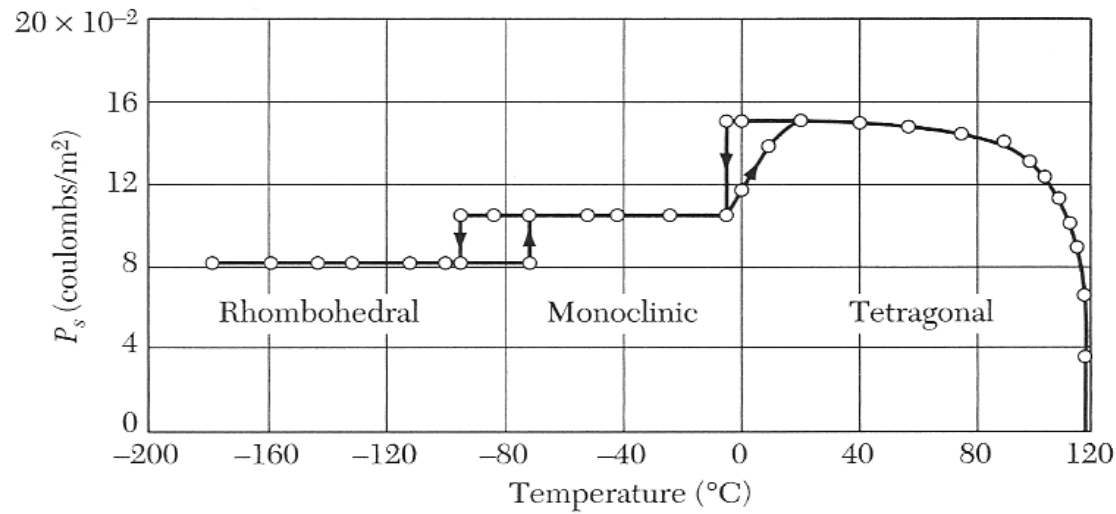
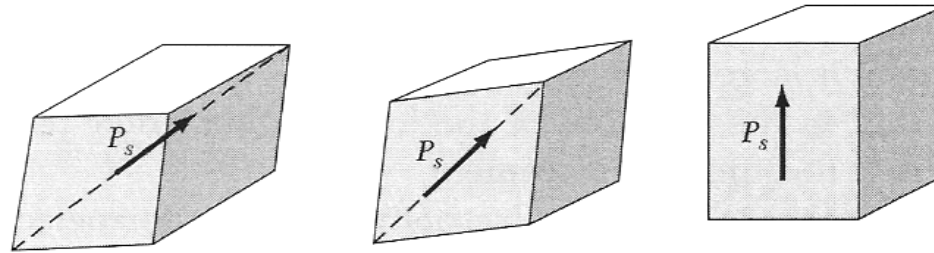
		T_c , in K	P_s , in $\mu\text{C cm}^{-2}$, at T K	
KDP type	KH_2PO_4	123	4.75	[96]
	KD_2PO_4	213	4.83	[180]
	RbH_2PO_4	147	5.6	[90]
	KH_2AsO_4	97	5.0	[78]
	GeTe	670	—	—
TGS type	Tri-glycine sulfate	322	2.8	[29]
	Tri-glycine selenate	295	3.2	[283]
Perovskites	BaTiO_3	408	26.0	[296]
	KNbO_3	708	30.0	[523]
	PbTiO_3	765	>50	[296]
	LiTaO_3	938	50	
	LiNbO_3	1480	71	[296]

Ferroelectric domains



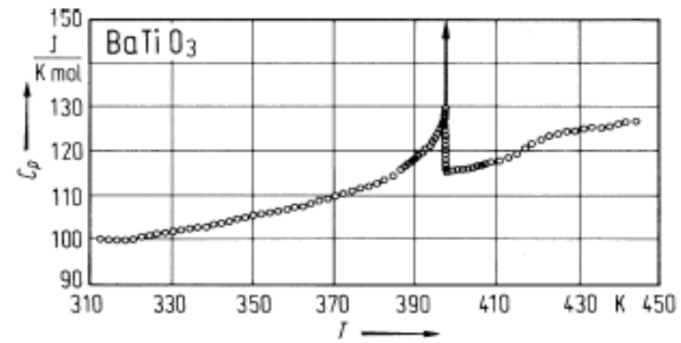
Increasing the electric field polarizes the material.

BaTiO₃



cubic (contains i = >
no spontaneous P)

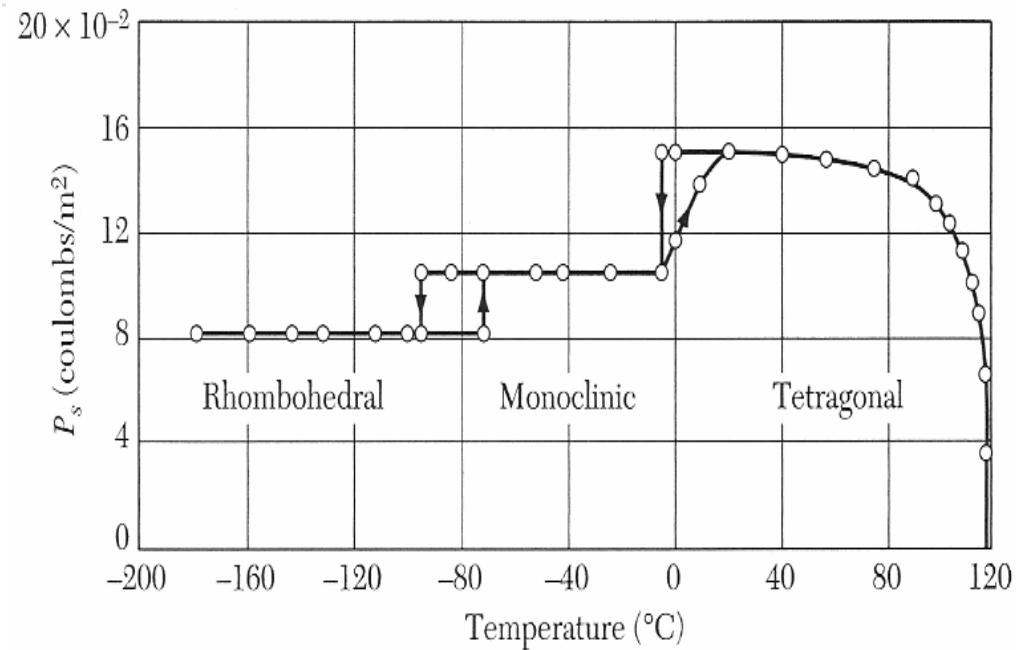
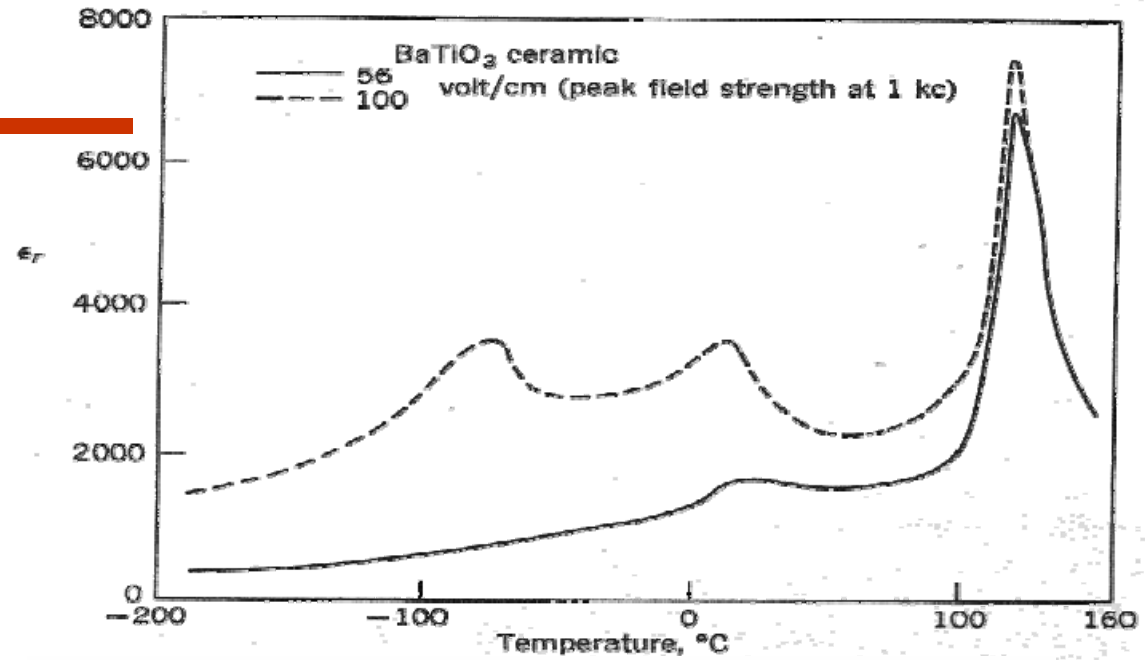
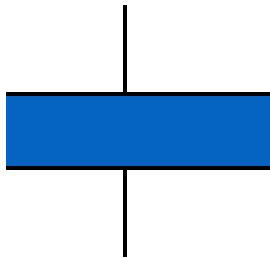
Can be used to make
nonvolatile memory



BaTiO₃

$$\epsilon_r = \chi + 1$$

Can be used to make
ultracapacitors

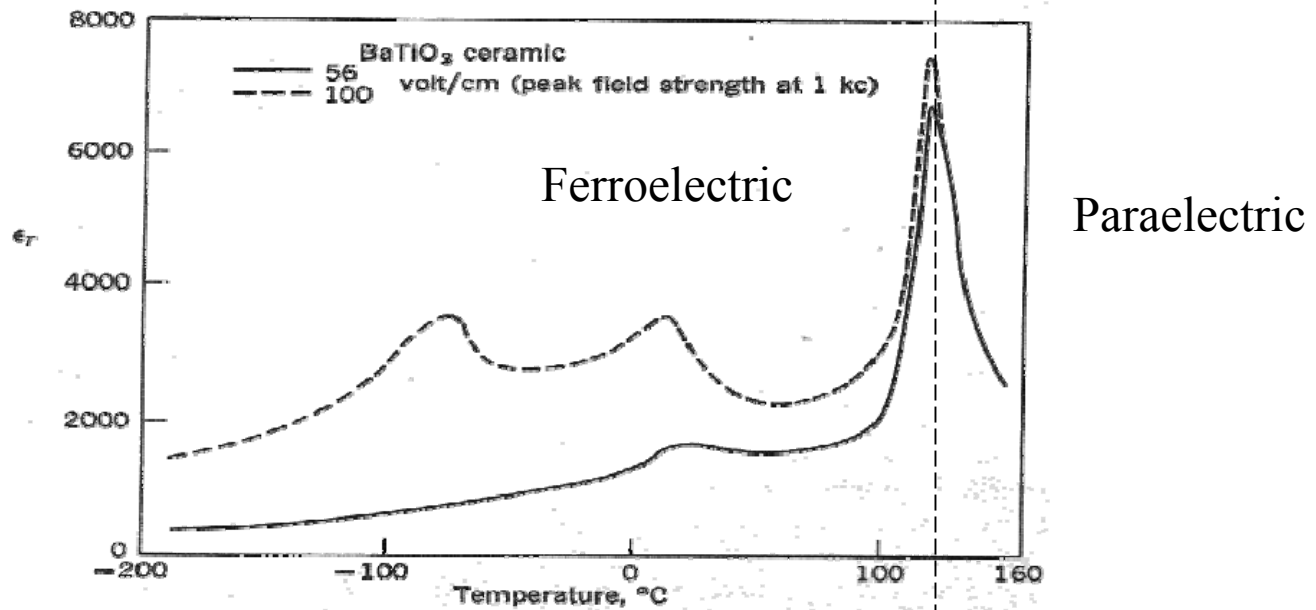


Paraelectric state

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

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

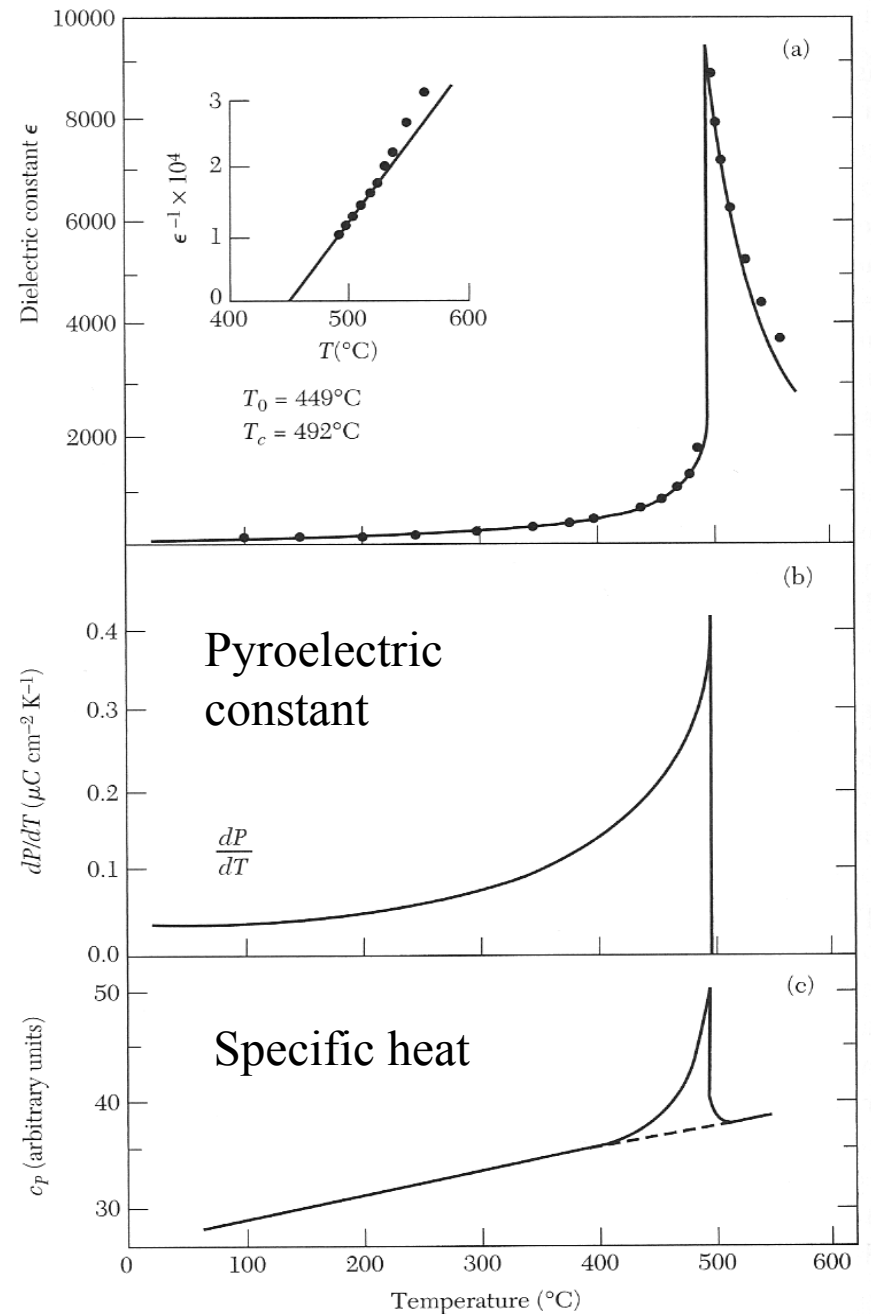
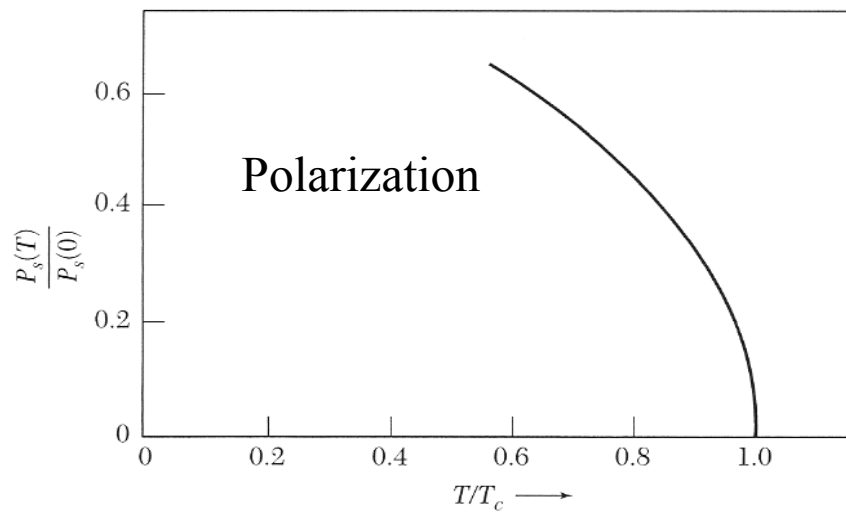
This causes a big peak in the dielectric constant at T_c .



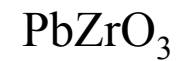
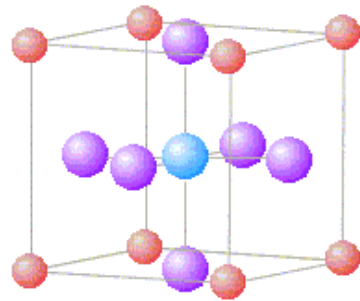
PbTiO₃

Dielectric constant

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



Antiferroelectricity

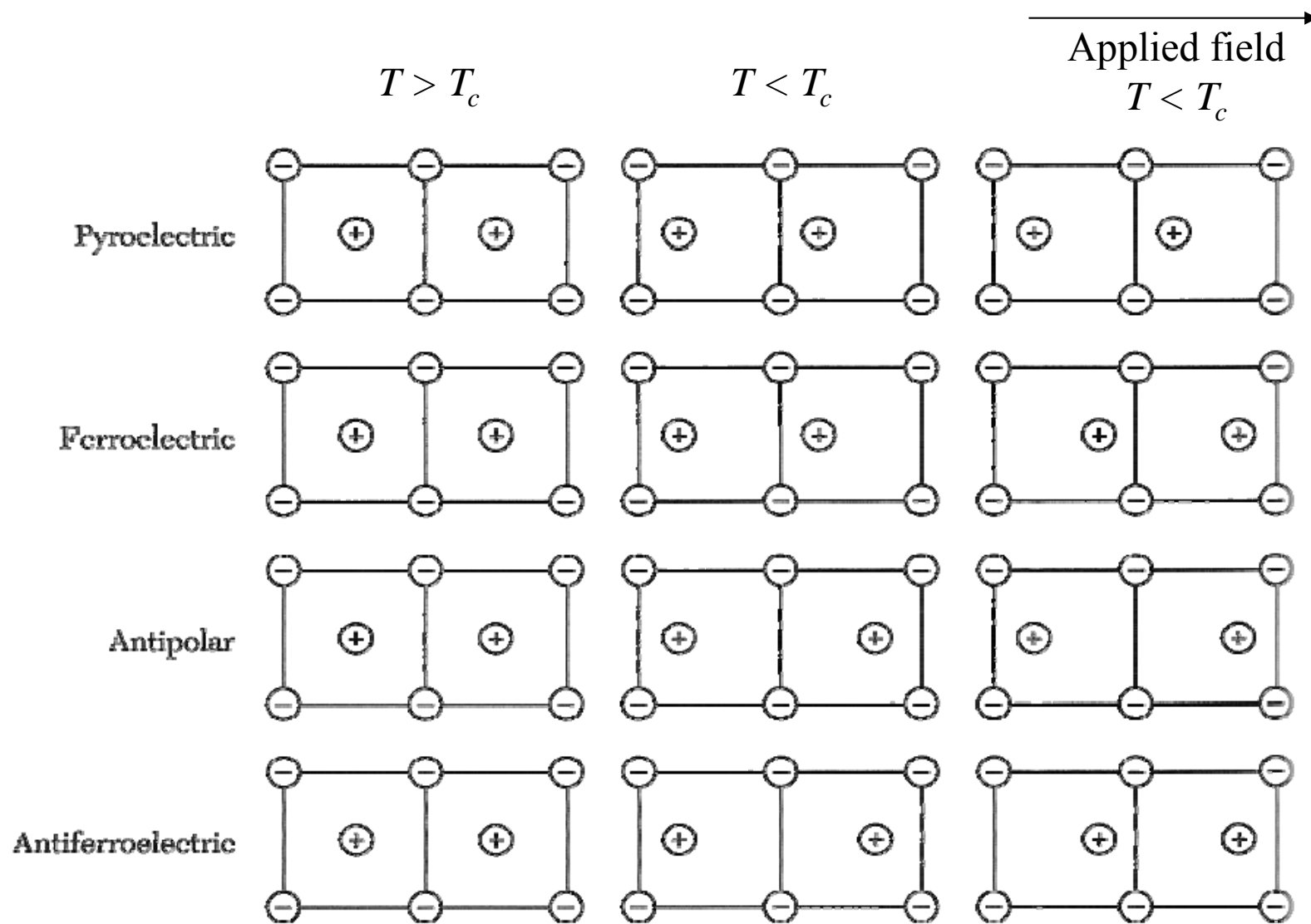


Polarization aligns antiparallel.

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

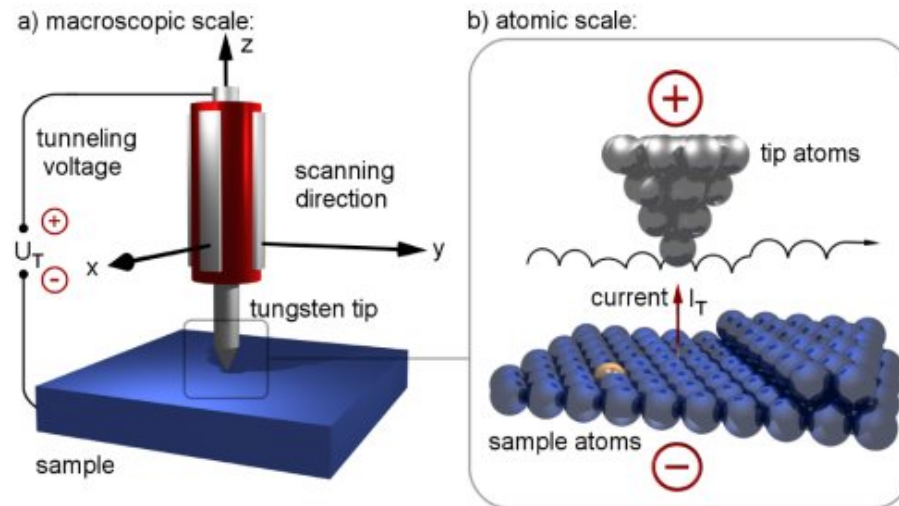
Gallium Orthophosphate (GaPO_4) $T_c = 970 \text{ K}$

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

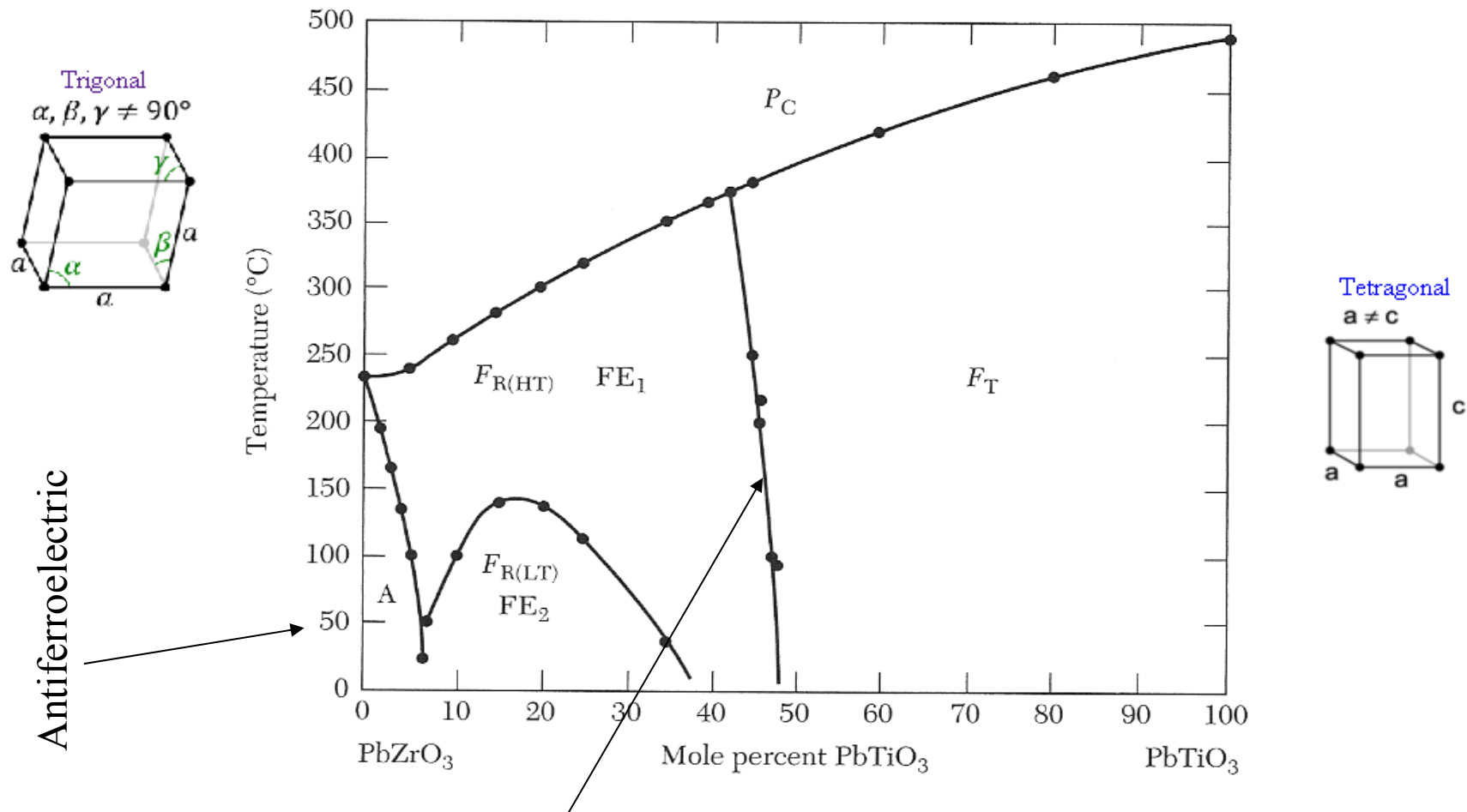
Piezoelectricity

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.

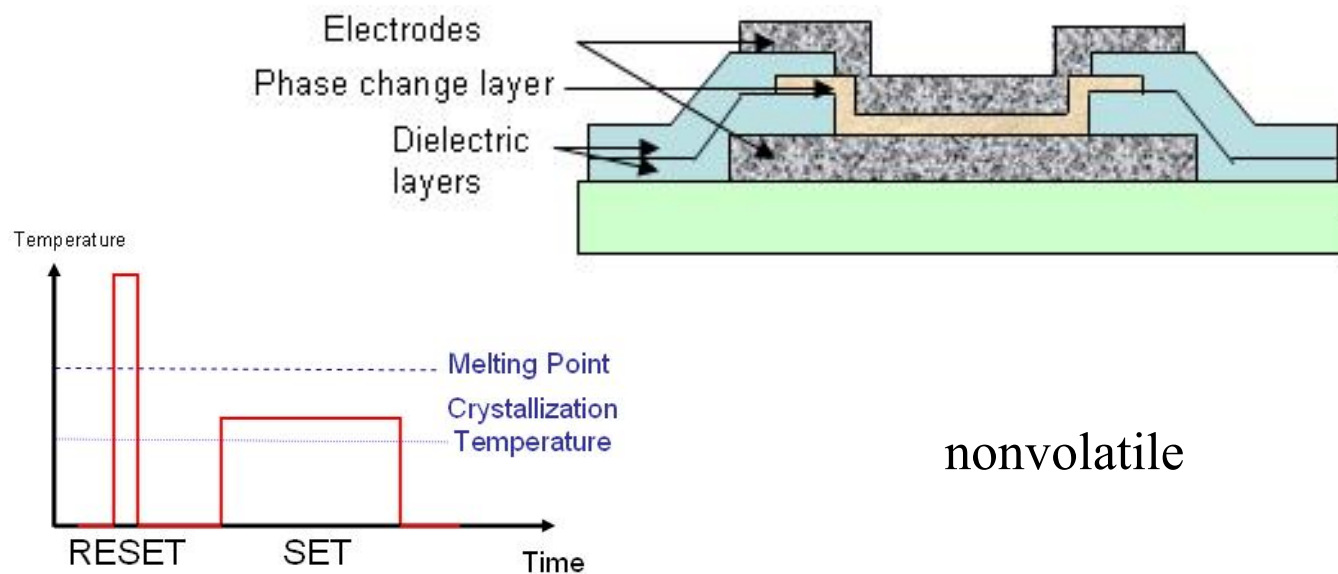
Superelasticity: Just above the transition temperature, the material exhibits elasticity 10-30 times that of an ordinary metal.

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.



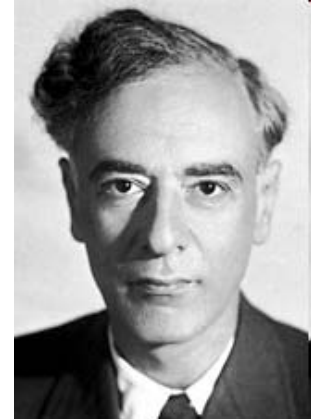
Landau Theory of Phase Transitions

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

Landau theory: order parameter

At a phase transition, an order parameter can be defined that is zero above the phase transition and nonzero below the phase transition.

Ferromagnetism	Magnetization
Ferroelectricity	Polarization
Superconductivity	Superconducting order parameter
Peierls Transition	amplitude of $2a$ distortion, gap
cubic-tetragonal structural	$c/a-1$ diffraction peak

1st and 2nd order phase transitions

First order:

There is a latent heat

order parameter increases discontinuously

water - ice

$$L = T(S_A - S_B)$$

Second order:

No latent heat

order parameter increases

continuously from zero

superfluidity

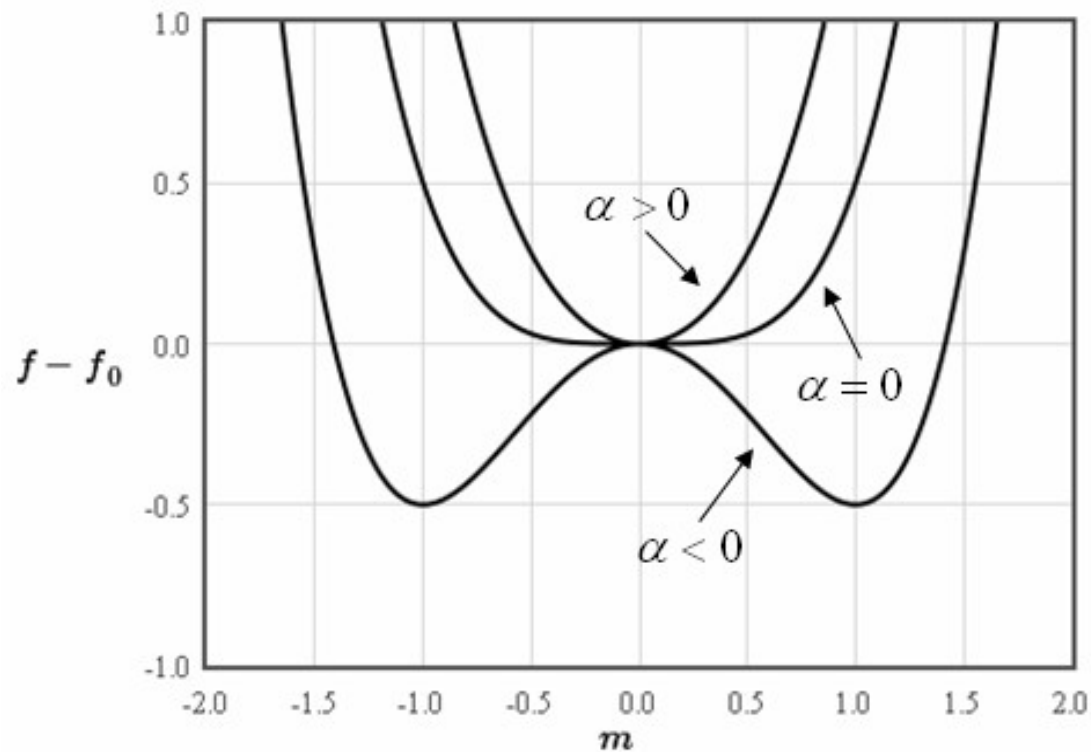
superconductivity

ferromagnetism

ferroelectricity

Peierls transition

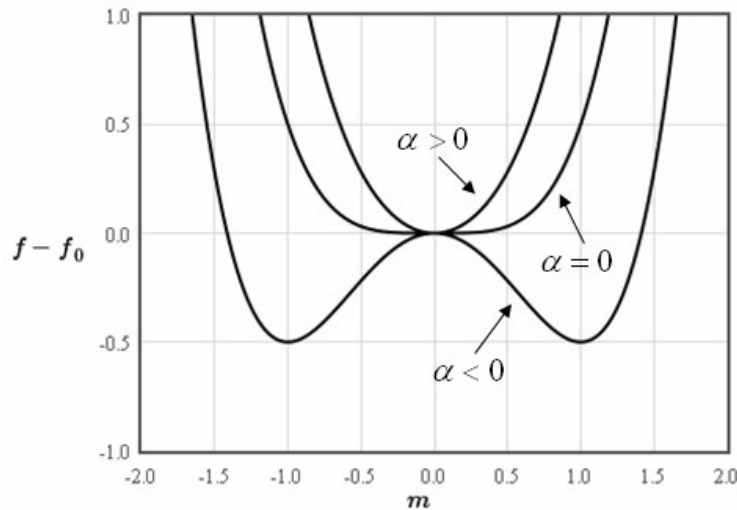
Expand the free energy in terms of the order parameter



$$f = f_0 + \alpha m^2 + \frac{1}{2} \beta m^4 + \dots$$

The odd terms are not physical.

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 .

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

The temperature dependence of the magnetization is

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