

Materials 218/UCSB: Class XIV: I and II order phase transitions: The example of BaTiO₃

Ram Seshadri (seshadri@mrl.ucsb.edu)

Background:

- Intrinsic stability of thermodynamic systems (after H. B. Callen, Thermodynamics and an introduction to thermostatistics, 2nd Edn.):

The entropy function S for a thermodynamic one-component system is:

$$S = S(U, V)$$

where U is the internal energy and V is the volume. By definition $dS = 0$ and $d^2S < 0$ describe equilibrium conditions. The first condition is that the entropy is at an extremum, and the second condition specifies that the extremum is a maximum.

If N is fixed, $S = S(U, V)$ and one can show by perturbing U and V slightly (both separately and together) that for the system to be *stable*, three conditions can be obtained:

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V \leq 0$$

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_U \leq 0$$

$$\left(\frac{\partial^2 S}{\partial U^2}\right)\left(\frac{\partial^2 S}{\partial V^2}\right) - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0$$

- Some of these conditions translate into more familiar ones. For example, suitable manipulation suggests that:

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = \frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_V = -\frac{1}{T^2 C_V} \leq 0$$

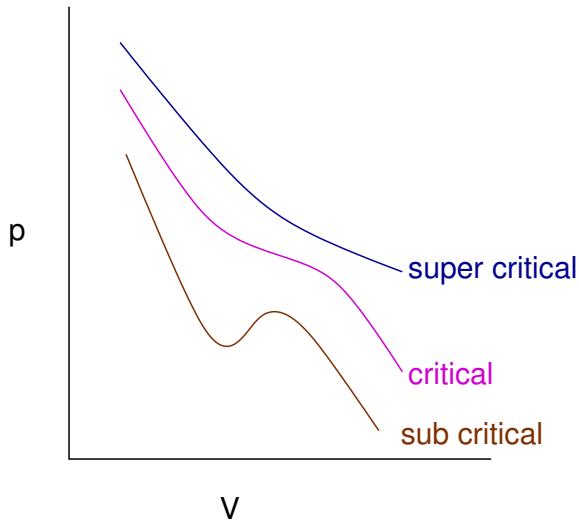
Which tell us, since T must always be positive, that C_V must always be positive for a system to be stable. In other words, when heat is provided to a system at constant volume, its temperature *must* increase.

Along the same lines, the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T > 0$$

If at constant T , pressure is applied on a system, the volume of the system *must* decrease.

There can exist regions in phase diagrams of 1-component system where the system might try and violate these stability conditions. Near these regions, *phase transitions* occur that prevent such violation.

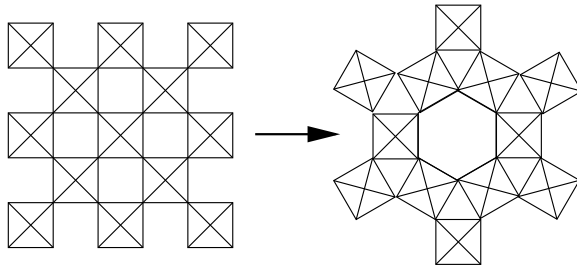


Consider isotherms of the van der Waals equation of state. In the lowest sub-critical trace shown above, there are regions which are clearly unstable as they correspond to regions with $\kappa_T < 0$. At these points, one can expect phase transitions.

- A study of phase transitions (or transformations) is particularly important in the solid state, since in many solid materials, properties (electrical, magnetic, mechanical ...) are inalienably linked with phase transitions that the material might have undergone, or might undergo.

Phase transitions and crystals (after Megaw):

- Reconstructive: There is complete fragmentation of the crystal associated with there being no orientational relationship between the parent and daughter phase:



An example is the phase transition from the perovskite lattice (left above) to the hexagonal tungsten bronze structure (right above). The A atoms in the structure are not shown.

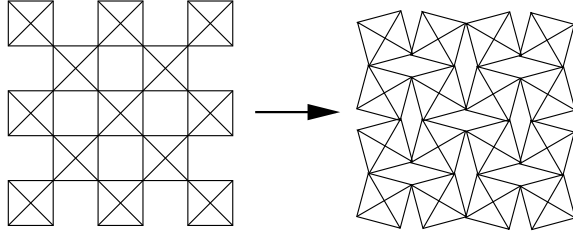
- Close orientational relationships; interchange of atoms, randomly, by diffusion: *Substitutional order-disorder*:

This is the kind of relationship seen on going from the $Fm\bar{3}m$ alloy $\text{Cu}_{0.75}\text{Au}_{0.25}$ with the Cu structure to the perovskite-like intermetallic $Pm\bar{3}m$ Cu_3Au . In the alloy, the fcc lattice sites are randomly occupied by (on average) $\text{Cu}_{0.75}\text{Au}_{0.25}$.

- No close orientational relationships, with large changes of shape; no diffusion: *Martensitic*:

This is the kind of phase transition that one has on going from the CsCl structure to the NaCl structure (happens to KI upon heating)

- Close orientational relationships: Pure displacive:
Obtained by mild shearing of structures. No bond-breaking or making. An example is going from a cubic perovskite to an orthorhombic perovskite:



- Close orientational relationships: Order-disorder by H hopping.
- Close orientational relationships: Orientational switching, ordering (eg C_{60}).
- Intra-atomic order disorder: Cooperative Jahn-Teller distortions, Verwey transitions.

The free energy across phase transitions and Landau theory:

Please see the handout.

BaTiO₃:

BaTiO₃ is one of the most widely used ferroelectric materials, and has been investigated in detail since its first preparation in the early 1940's. Above 393 K, it is cubic, and has the ideal perovskite structure. It is paraelectric, meaning that electric polarization (the number of electric dipoles per unit volume) increase linearly with the applied electric field.

The *tolerance* factor of BaTiO₃ defined:

$$t = \frac{(r_{\text{Ba}} + r_{\text{O}})}{\sqrt{2}(r_{\text{Ti}} + r_{\text{O}})}$$

is greater than 1 (it is 1.07) which means that Ba²⁺ is too large to fit into the space created by eight TiO₆ octahedra at the corners of the perovskite cube. In addition, Ti⁴⁺ has the d^0 configuration. This is a configuration prone to go *off-center* which is good for ferroelectricity.

Please see the handout for more on BaTiO₃.