Differences/Difficulties of Calorimetry Measurements of 1st and 2nd Order Transitions

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Heat Capacity and Calorimetry Techniques

- Heat Capacity:
  \[ \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial Q}{\partial T} \right)_P = C_P \]

- Power supplied over time interval \( (P(t)) \) to achieve temperature change
  \[ \int_{t_0}^{t} P(t)\,dt = \int_{T_0}^{T} C_s(T)\,dT = Q \]
  - Heat capacity may be determined

Heat Capacity and Calorimetry Techniques

- Including, but not limited to:
  - Low Temperature Heat Capacity
    - Relaxation (QD PPMS)
    - AC modulation
  - High temperature calorimetry
    - Differential scanning calorimetry

A little history...

- Ehrenfest: First-order, second-order definition based on continuity of partial differentials (1933)

- Disputed by Justi and Laue – insisted there is no thermodynamic/experimental justification for second-order (1934)

- Landau developed a theory to demonstrate such second-order phase transitions (originally reported in 1935 but later published in Statistical Physics text in 1969)
First and Second Order Phase Transitions

**First-Order** (Discontinuous):

\[
\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad \left(\frac{\partial G}{\partial p}\right)_T = V
\]

- Latent heat is absorbed or released

**Second-Order** (Continuous):

\[
\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\frac{c_p}{T}, \quad \left(\frac{\partial^2 G}{\partial p^2}\right)_T = -V\kappa_T, \quad \left(\frac{\partial^2 G}{\partial T \partial p}\right) = V\beta_p
\]

- No latent heat

First-order:
- Breaking and making of bonds – change in G
- Drastic “jump” at phase transition temperature ($T_c$)
- Originally labeled as “normal”

Second-order:
- No change in coordination of atoms in structure
- Change in enthalpy from lattice distortions – no broken bonds
- A continuous change from one phase into another
Low Temperature Heat Capacity

- Must be careful for any parasitic heat contributions

- Relaxation measurements (QD PPMS)
  - Not good for 1\textsuperscript{st} order phase transitions
  - Limited by relaxation time scales
  - Need flat and relatively thin samples (for best thermal contact possible)

- AC modulation heat capacity
  - Uses temperature oscillations of a particular frequency
  - Would like to minimize addendum contribution – materials chosen are important

High Temperature Calorimetry Example

- Differential Scanning Calorimetry uses difference between a blank and a sample

- Difference of voltage input required for reference vs sample measured
  \[ \Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}} \]

Difficulties to consider with phase transitions

- Flow of latent heat may cause hysteresis of signal
  - Causing λ shape in $C_p$ curve
- There may be cracking in the sample
  - Leading to bad thermal connections
- Temperature-dependence near transition temperatures may change depending on domains and domain boundaries present in the sample
- Magnetic phase transitions may provide additional complexity
Examples

First Order

Second Order

More Complex Examples


Triglycine selenate = TGSe
The $\lambda$ anomaly

- Need both heating and cooling curves to detect any possible hysteresis
  - Old techniques of “adiabatic calorimetry” were one-way only measurements
- Differential Scanning Calorimetry displays both ascending and descending runs with proper endo- or exothermic peaks

Thank you!