Thermal analysis – heat capacity

590B F08

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Detour – phase transitions of 2 ½ order
Heat capacity
2 ½ order phase transition

aka: electronic topological transition (ETT), Lifshitz transition


also:

2 ½ order phase transition

electronic DOS \quad \varrho(\varepsilon) = \varrho_0(\varepsilon) + \delta \varrho

\delta \varrho = \begin{cases} 0, & \text{region I,} \\ \alpha |\varepsilon - \varepsilon_c|^{1/2}, & \text{region II,} \end{cases}

\alpha = N\varepsilon^{-1/2}, \text{ and } N \text{ is the electron concentration in the metal parameter:} \quad Z_0 = \varepsilon_F - \varepsilon_c

thermodynamic potential

\delta \Omega_c = \begin{cases} 0, & \text{region I,} \\ -(4/15)\alpha |Z|^{5/2}, & \text{region II.} \end{cases}

T=0, \text{ no scattering}
2 ½ order phase transition

Li-Mg alloy

\[ \delta \Omega_e = \begin{cases} 
- \left( \frac{\pi}{2} \right)^{1/2} \alpha T^{5/2} \exp \left( - \frac{|Z|}{T} \right), & \text{region I}, \\
- \frac{4}{15} \alpha |Z|^{5/2} - \frac{\pi^2}{6} \alpha T^2 |Z|^{1/2}, & \text{region II}. 
\end{cases} \]

low temperature, no scattering

ALSO other control parameters
2 ½ order phase transition

LSCO high-$T_c$ SC

QCP in heavy fermions

New box – the same good old taste
Heat capacity

\[ C_p = \left( \frac{dQ}{dT} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p \]
\[ C_v = \left( \frac{dQ}{dT} \right)_v = T \left( \frac{\partial S}{\partial T} \right)_v \]
\[ C_p - C_v = TV\beta^2/k_T \]

Q – heat, \( S \) - entropy

\( \beta \) – volume thermal expansion, \( k_T \) – isothermal volume compressibility

For solids \( C_p \sim C_v \)

Usually we measure \( C_p \)
Heat capacity – WHY?

* Useful knowledge for useful (structural) materials – how easy to cool down

* To learn something about electrons and phonons

\[ T \rightarrow 0: \quad C_p = \gamma T + \beta T^3 \] (no magnetism)

\( \gamma \sim N(0)(1 + \lambda) \) - electronic density of states

\( \lambda \) - measure of e-e (and e-phonon) interactions, \( m^*/m_0 = (1 + \lambda) \)

\( \gamma > 400 \text{ mJ/mol K}^2 \) – “heavy fermions” – an enormous, separate research field that entertains number of us

\[ \Theta_D = (1944/\beta)^{1/3} \] - Debye temperature (use right units)

 tells you something about stiffness of the lattice, helps to understand BCS superconductors \( [T_c \sim \Theta_D \exp(-1/N(0)V)] \)
Lattice heat capacity – Debye and Einstein

**Einstein – single frequency**

\[
C_v\left(\frac{\Theta_E}{T}\right) = 3sR\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E / T)}{[\exp(\Theta_E / T) - 1]^2}
\]

\[
C_v = 3sR\left(\frac{\Theta_E}{T}\right)^2 \exp\left(-\frac{\Theta_E}{T}\right) + \ldots \quad (T \ll \Theta_E)
\]

\[
C_v = 3sR\left[1 - \frac{1}{12}\left(\frac{\Theta_E}{T}\right)^2 + \ldots \right] \quad (T >> \Theta_E)
\]

**Debye – elastic continuum**

\[
C_v = 9Rs\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} x^4 e^x dx (e^x - 1)^2 = 9Rs (T/\Theta_D)^3 D(\Theta_D / T)
\]

\[
C_v = \frac{12\pi^4}{5} (Rs/\Theta_D^3) T^3 = \beta_3 T^3 \quad (T << \Theta_D)
\]

\[
C_v = 3sR\left[1 - \frac{1}{20}\left(\frac{\Theta_D}{T}\right)^2 + \ldots \right] \quad (T >> \Theta_D)
\]
Lattice heat capacity – Debye and Einstein

One can also use realistic phonon DOS and calculate $C_p$

- Debye
- Einstein

![Graphs showing Debye and Einstein heat capacity models](image)

- Blackman
- "realistic"

Novel Materials and Ground States
Heat capacity – WHY?

- To learn something about magnons

Ferro (ferri) magnets

Isotropic

\[ C_M = s_f R \left( \frac{k_B T}{2JS} \right)^{3/2} \]

Anisotropic

\[ C_M \sim T^{3/2} \exp \left( - \frac{E_g}{k_B T} \right) \]

Antiferromagnets

Isotropic

\[ C_M = s_{af} R \left( \frac{k_B T}{2J' S} \right)^{3} \]

Anisotropic

\[ C_M \sim T^{3} \exp \left( - \frac{E_g}{k_B T} \right) \]

And need to remember contributions from electrons and phonons: \( C_p = \gamma T + \beta T^3 \)
Heat capacity – WHY?

• To learn something about superconductors

\[ C_S \sim \exp\left(-1.76 \frac{T_c}{T}\right) \]
Heat capacity – WHY?

• To learn something about superconductors

MgB$_2$

Two-gap superconductor
Heat capacity – WHY?

- To learn something about crystal electric field (Schottky anomaly)

\[ C_{\text{Sch}} = R \left( \frac{\Delta}{T} \right)^2 \frac{(g_0 / g_1) \exp(\Delta / T)}{[1 + (g_0 / g_1) \exp(\Delta / T)]^2} \]

\[ C_{\text{Sch}} = R \left( \frac{g_1}{g_0} \right) \left( \frac{\Delta}{T} \right)^2 \exp \left( - \frac{\Delta}{T} \right) \quad T \ll \Delta \]

\[ C_{\text{Sch}} = R \frac{g_0 g_1}{(g_0 + g_1)^2} \left( \frac{\Delta}{T} \right)^2 \quad T \gg \Delta \]

\[ \exp \left( - \frac{\Delta}{T_m} \right) = \left( \frac{g_1}{g_0} \right) \frac{(\Delta / T_m) + 2}{(\Delta / T_m) - 2} \]

maximum:

\[ C_{\text{Sch}}(\text{max}) = R \left[ \left( \frac{\Delta}{2T_m} \right)^2 - 1 \right] \]
Heat capacity – WHY?

- To learn something about spin glasses

\[
\frac{C_m}{c} = \Gamma \left( \frac{T}{c} \right) \quad \text{Scaling hypothesis}
\]
Heat capacity – WHY?

• To learn something about spin glasses

\[ \frac{1}{T} \]

\[ T_{max} \approx 1.5 T_f \]
Heat capacity – WHY?

- To learn something about magnetic transitions

Also can play entropy game and evaluate degeneracy of the ground state

\[ \Delta S_m = R \ln N \]
Heat capacity – HOW?

- relaxation (QD PPMS)

\[ C_{\text{total}} \frac{dT}{dt} = -K_w(T - T_b) + P(t), \quad \text{simple} \]

\[ C_{\text{platform}} \frac{dT_p}{dt} = P(t) - K_w(T_p(t) - T_b) + K_g(T_s(t) - T_p(t)) \]

\[ C_{\text{sample}} \frac{dT_s}{dt} = -K_g(T_s(t) - T_p(t)), \quad \text{more realistic} \]

fit with two exponents
Heat capacity – HOW?

• relaxation (QD PPMS)

calibrated heater and thermometer
sophisticated temperature control and fitting software
need to measure addenda (platform + grease) every time
need to calibrate heater and thermometer in magnetic field
need to shape your sample
vertical 3He platform may oscillate in magnetic field
remember about torque
assembly is fragile

measurements take long time
not good for 1st order phase transitions
Heat capacity – HOW?

• ac modulation

\[ \tau_1 \text{ – sample to bath; } \]
\[ \tau_2 \text{ – response time of the sample } \]

\[ T_{ac} = \frac{\text{Power}}{2\omega C(1 + 1/\omega^2 \tau_1^2 + \omega^2 \tau_2^2 + \text{const})^{1/2}}. \]

if \( \tau_2 \ll 1/\omega \ll \tau_1 \)

\[ C = \frac{\text{Power}}{2\omega T_{ac}(1 + \text{const})^{1/2}}. \]

Heat capacity – HOW?

• ac modulation

fast
scalable, good for small sample
accurate (relative measurements)
can use e.g. in pressure cells

hard to get absolute values
Reading:

Quantum Design Manual and refs therein

E.S.R. Gopal, Specific heats at low temperatures.

A.Tari, Specific heat of matter at low temperatures.

T.H.K. Barron and G.K. White, Heat capacity and thermal expansion at low temperatures.