

Specific Heat of Solids – Part 1



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According to the first law of thermodynamics

$$dQ = dE + pdV \quad (1)$$

Where dQ is the amount of heat added and dE is the increase in the energy of system $E(T,V)$. Now E can be determined uniquely by the temperature and volume of the system. Hence,

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad (2)$$

$$dQ = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] dV \quad (3)$$

Specific heat is defined by dQ/dT . The specific heat at constant volume is :

$$\left(\frac{\partial Q}{\partial T}\right)_V = C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad (4)$$

C_V is more important than C_p because it can be measured easily.

The second law leads to the following relation between C_p and C_V .

$$C_p - C_V = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial p}{\partial V}\right)_T \quad (5)$$

Equation (5) may be rewritten in terms of volume expansion coefficient α_V and compressibility K , defined by –

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p, \quad K = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Equation (5) then takes the form -

$$C_p - C_V = \alpha_V^2 TV / K$$

Since both α_V and K , are positive quantities

$$C_p - C_V \geq 0$$

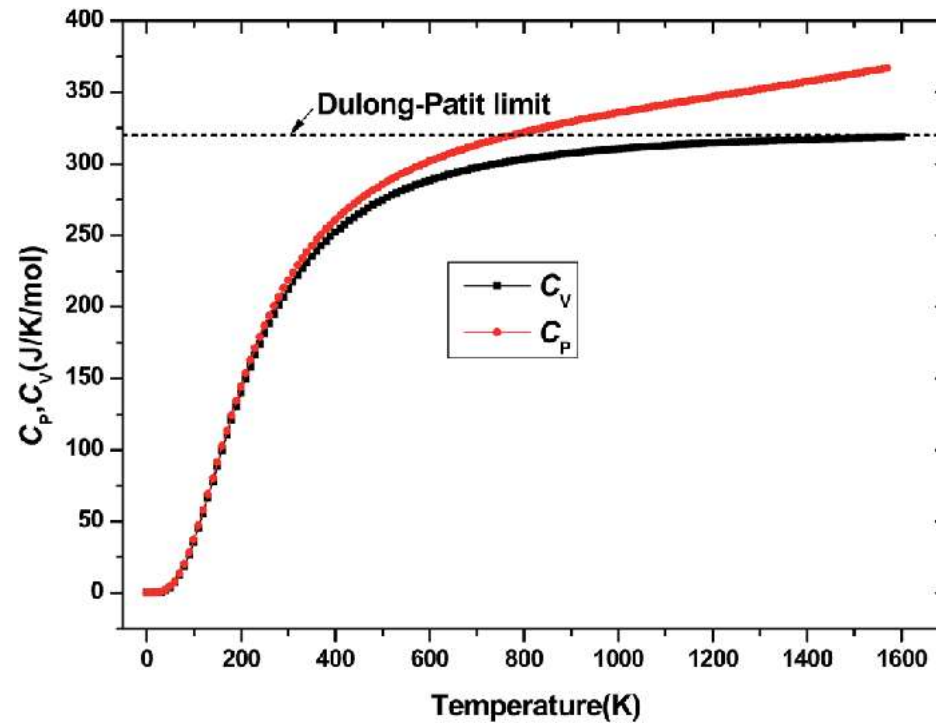
The temperature variation of C_P and C_V is shown at low temperature the difference between C_P and C_V becomes zero. At

$$T = 0\text{K}, C_p = C_V \approx 0$$

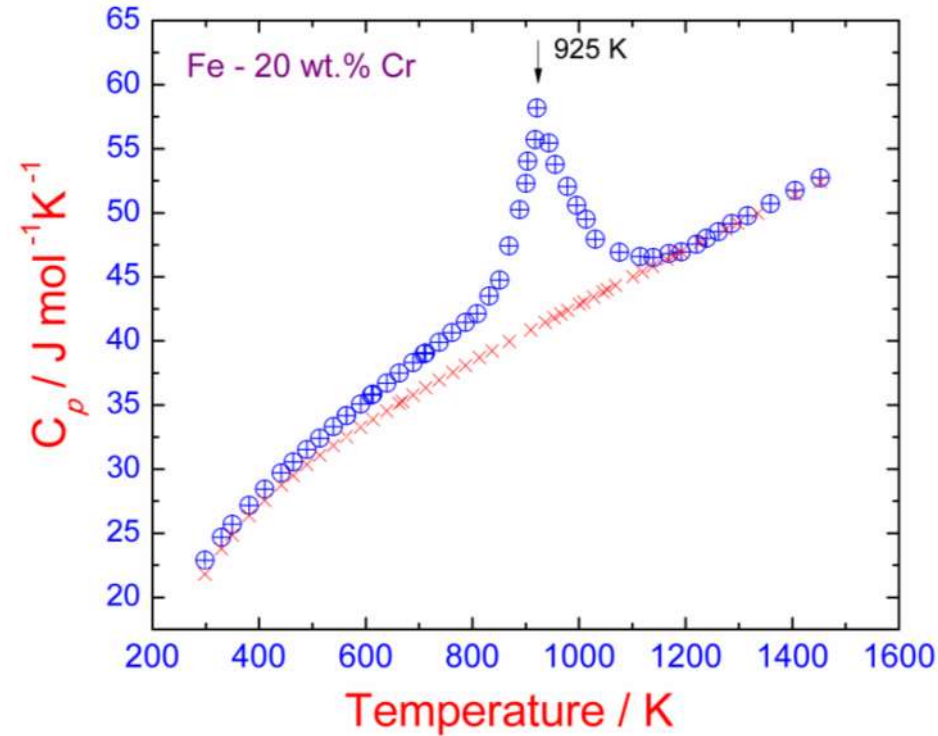
$$C_p - C_V \propto T \text{ (function of temperature)}$$

The contribution to the heat capacity:

- Atomic vibrations in the crystal
- In metals and semiconductor – contribution from electronic systems. Usually this contribution is small relative to lattice vibrations.



As temperature is raised from absolute zero the heat capacity increases drastically and finally reaches a nearly constant value. For elements the value at high temperature is 6 cal/ mole/ degree. This is known as Dulong Petit law.



Anomaly in specific heat curves is observed in the ferromagnetic metals like Ni, Co, Fe etc. A peak is observed in the vicinity of Curie temperature. The peak is associated with the transition from the ferromagnetic (ordered) to the paramagnetic (disordered) state.

Various theories of lattice heat capacity:

It was considered that vibrational energy of linear chain of N atoms may be expressed as the energy of N harmonic oscillators. For 3-D lattice it is equal to the energy of a system of $3N$ oscillators. The differences between different theories are based on their differences in the proposed frequency spectrum of oscillators.

- Dulong-Petit Law (classical theory)
- Einstein theory
- Debye Theory
- Born's modification to Debye Theory