Lattice specific heat: general information

Specific heat – the ratio of an infinitesimal amount of heat δQ per unit mass obtained by the sample to the corresponding infinitesimal increase of its temperature δT:

$$C = \frac{\delta Q}{\delta T} \; .$$

In an experiment the specific heat is usually determined under constant pressure.

In theory the specific heat is calculated under constant volume.

These two quantities are related as follows.

The following thermodynamic relation

$$C_p - C_V = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T$$

allows us to express the difference $C_p - C_V$ in measurable quantities, the volume expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and the isothermal compressibility coefficient

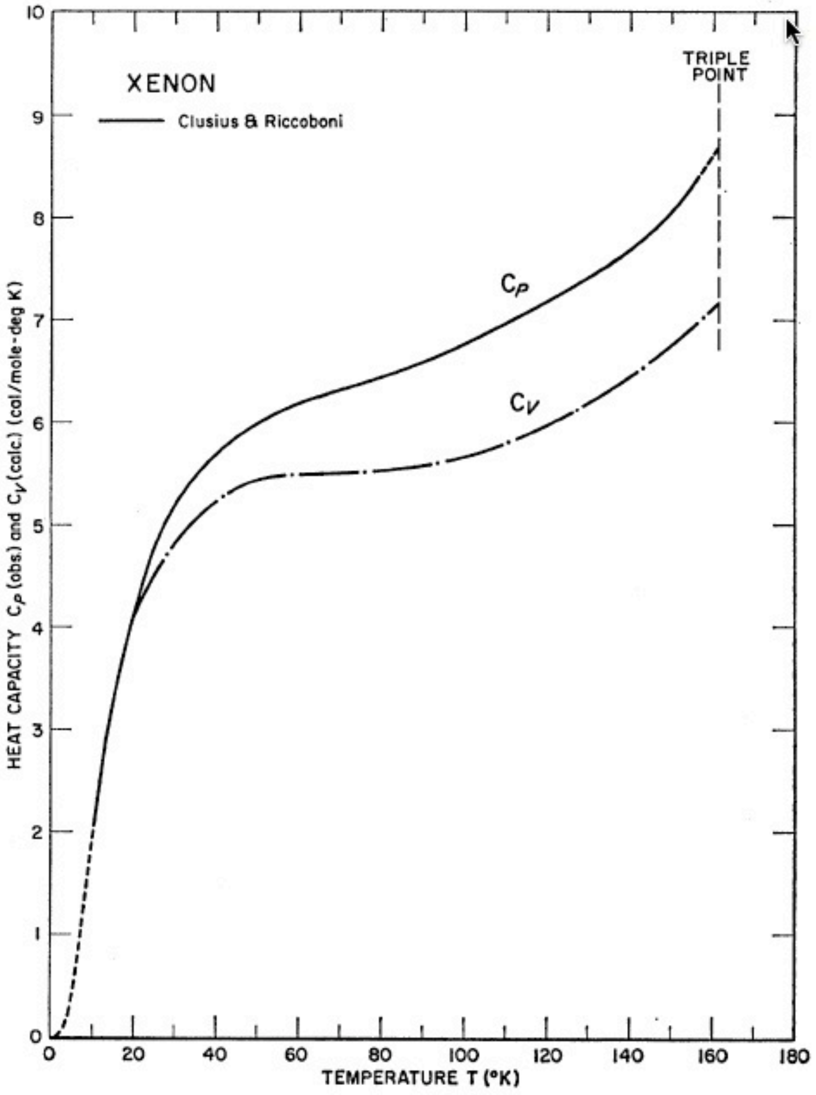
$$B = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad .$$

We obtain

$$C_p - C_V = \frac{\alpha^2}{B} TV. \quad (5.10)$$

The difference $C_p - C_V$ increases with increasing temperature. See, for example, the specific heat data for solid Xe.

At high temperatures C_V is close to the Dulong–Petit value of $3R$.



[from G. L. Pollack, Rev. Mod. Phys. **36**, 748–791 (1964)]

Specific heat measurements

The adiabatic method

Traditional adiabatic calorimeters employ a variety of methods to isolate the sample from its surroundings.

The specific heat is determined from the temperature rise ΔT, when heat ΔQ is applied to the sample:

$$C = \Delta Q / \Delta T \quad .$$

AC—the most precise method (although the oldest)

pros—stat. error $\leq$ 0.1%, abs. accuracy 0.5–0.8%

cons—large samples

The ac temperature method (Sullivan and Seidel, 1968)

Heat is applied at a frequency ω. If P_ω is the ω component of the heat applied, the ω component of the temperature rise is

$$(\Delta T)_\omega = P_\omega / \omega C \ .$$

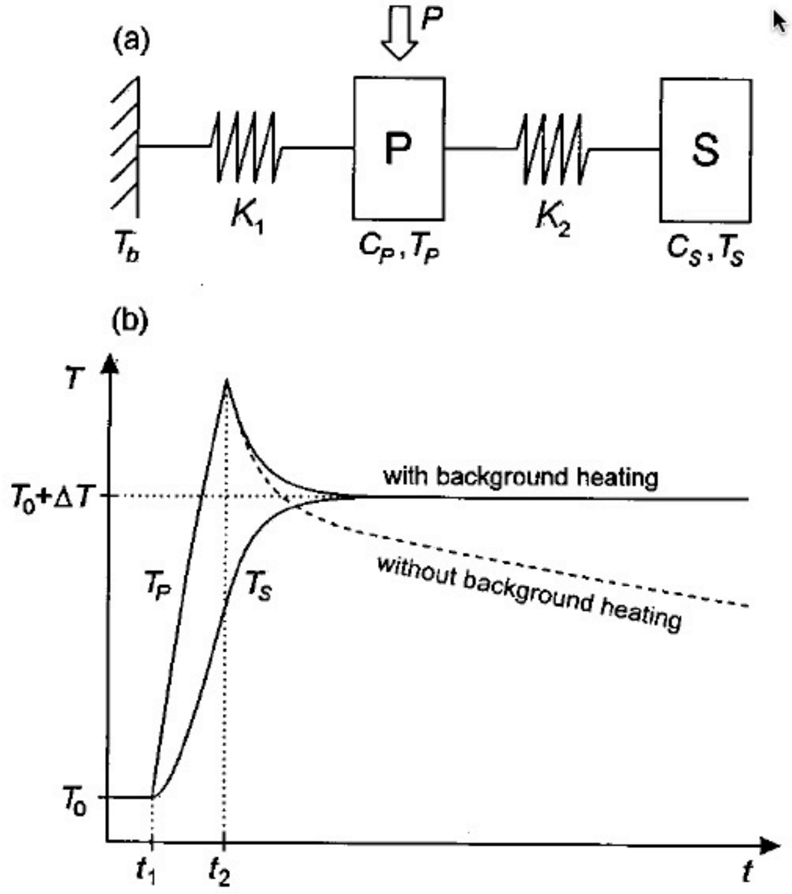
Long relaxation times are no longer needed.

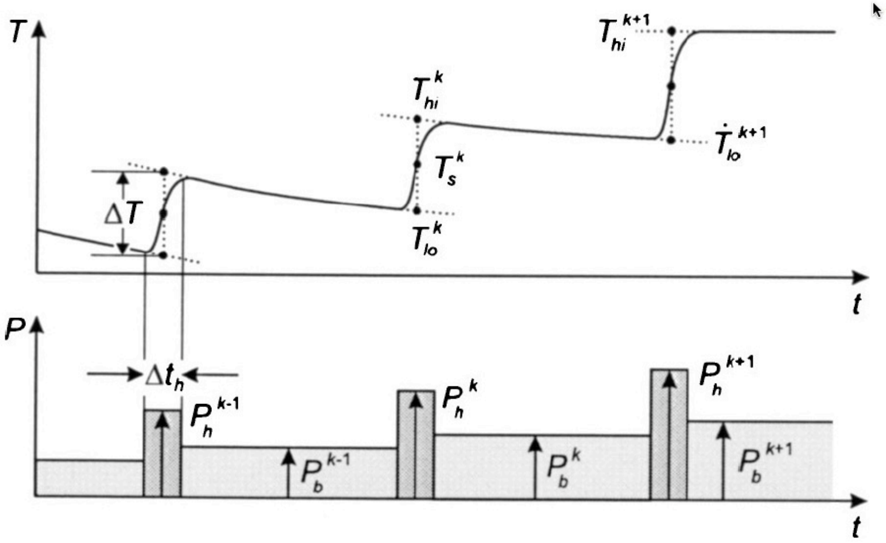
The pulsed calorimeter (Morin and Maita, 1963)

pros—small samples in the 200 mg range

The compensated heat-pulse method (Wilhelm *et al.*, 2004)

pros—small samples, fast data acquisition

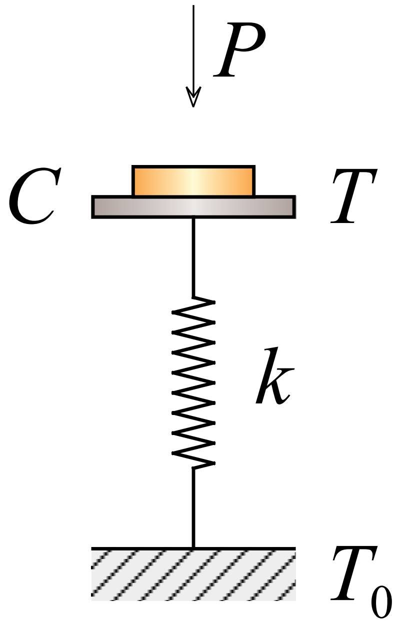




[from H. Wilhelm, T. Lühmann, T. Rus and F. Steglich, Rev. Sci. Instr. **75**, 2700 (2004)

The relaxation method (Bachmann *et al.*, 1972)

In steady state power P flows through the set-up. When power is cut off, the temperature decays from T_1 to T_0 with a time constant C/k, where k is the thermal conductance of a link between the sample and the heat reservoir.



The specific heat is given by

$$C = -\frac{k\left(\bar{T}\right)}{d\left(\ln \Delta T\right)/dt} \;,$$

where $\bar{T} = \frac{1}{2}(T + T_0)$ and $\Delta T = T - T_0$.

If C is temperature independent between T_1 and T_0, we find

$$\frac{d \ln \Delta T}{dt} = -\frac{1}{\tau} = -\frac{k}{C}$$

and

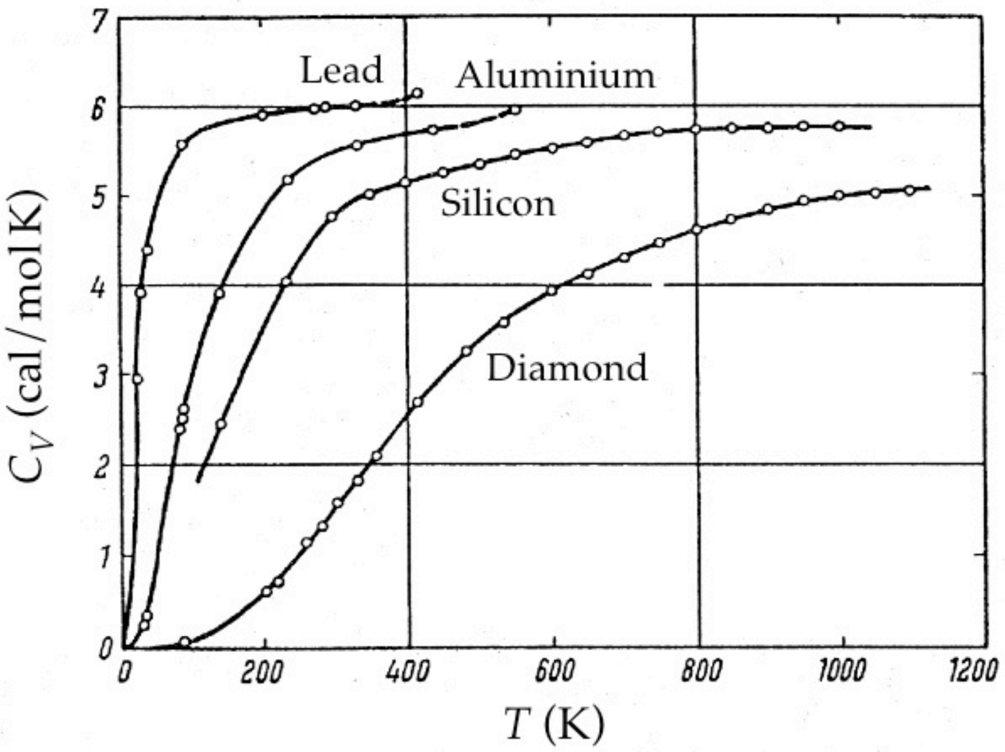
$$\Delta T(t) = (T_1 - T_0) e^{-t/\tau} \quad .$$

The specific heat is determined from the measured values of k and τ.

pros—low temperatures, small samples (1 mg range)

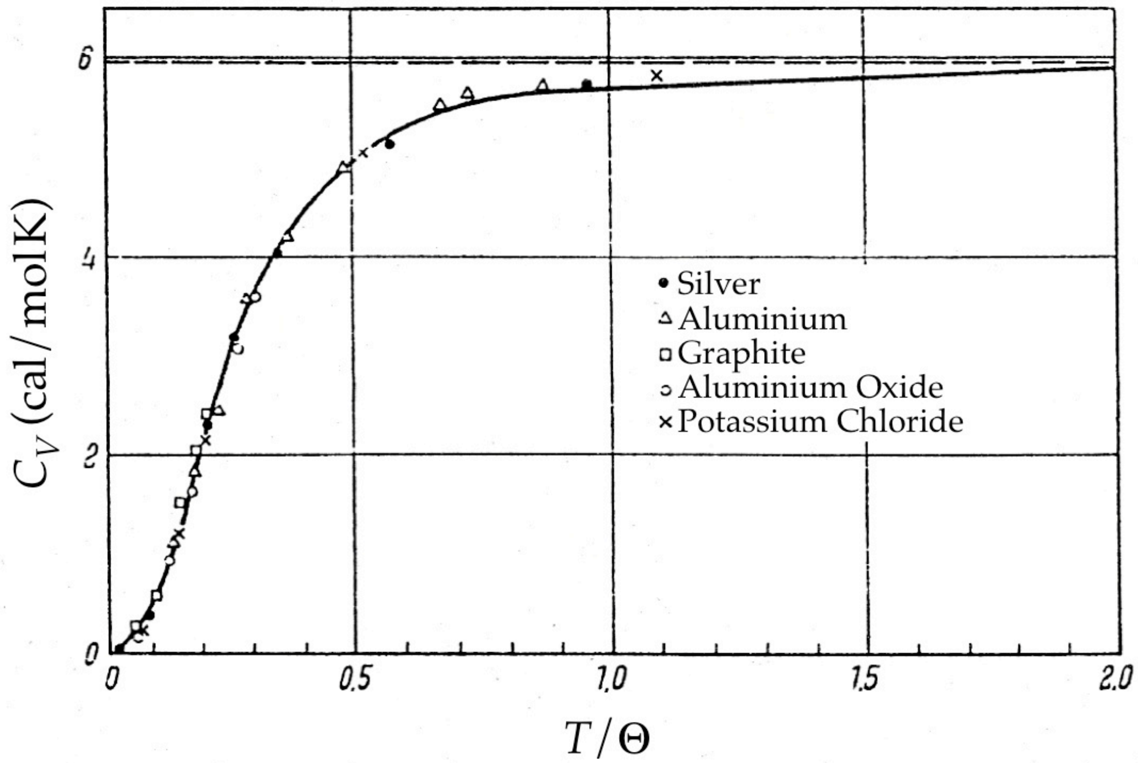
Commercial instruments available (PPMS, Quantum Design)

The $C_V(T)$ variations for different solids are quite similar.



[from F. K. Richtmyer, E. H. Kennard and J. N. Cooper, *Introduction to Modern Physics*, 6th ed. (McGraw-Hill, New York, 1969)]

If the C_V is plotted vs. T/Θ, then the specific heat data for different solids collapse into a universal curve.



[from F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, New York, 1940)]

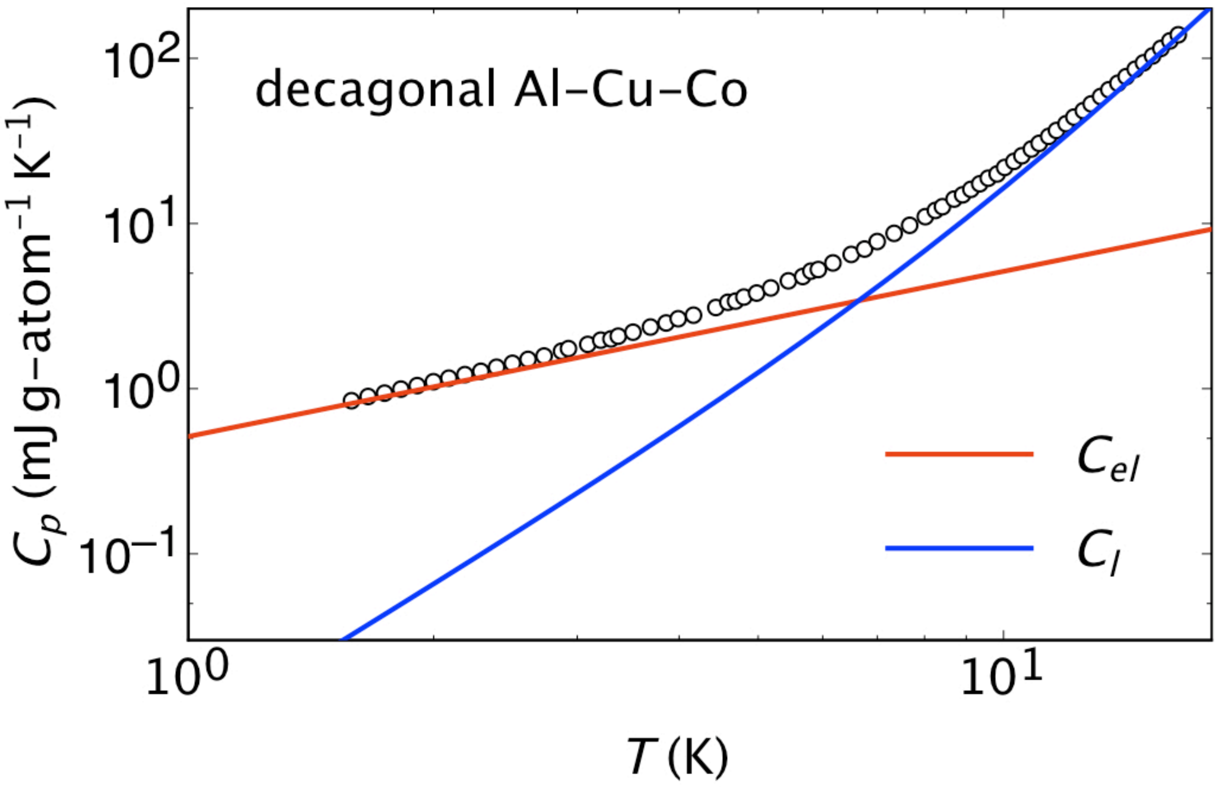
The characteristic temperature Θ plays an important role, which we will discuss later.

As it appears, it does not matter if the solid contains atoms of just one type or of many types.

Experiment: in the temperature range $T/\Theta \ll 1$ the specific heat of insulators varies with the temperature as T^3, and in this temperature range the difference $C_p - C_V$ can be neglected.

The specific heat of metals contains an additional contribution to C_V, due to the thermal excitation of itinerary electrons.

The electronic contribution to C_V linearly increases with increasing temperature; it is important (comparable to the lattice contribution), however, only up to several Kelvin.

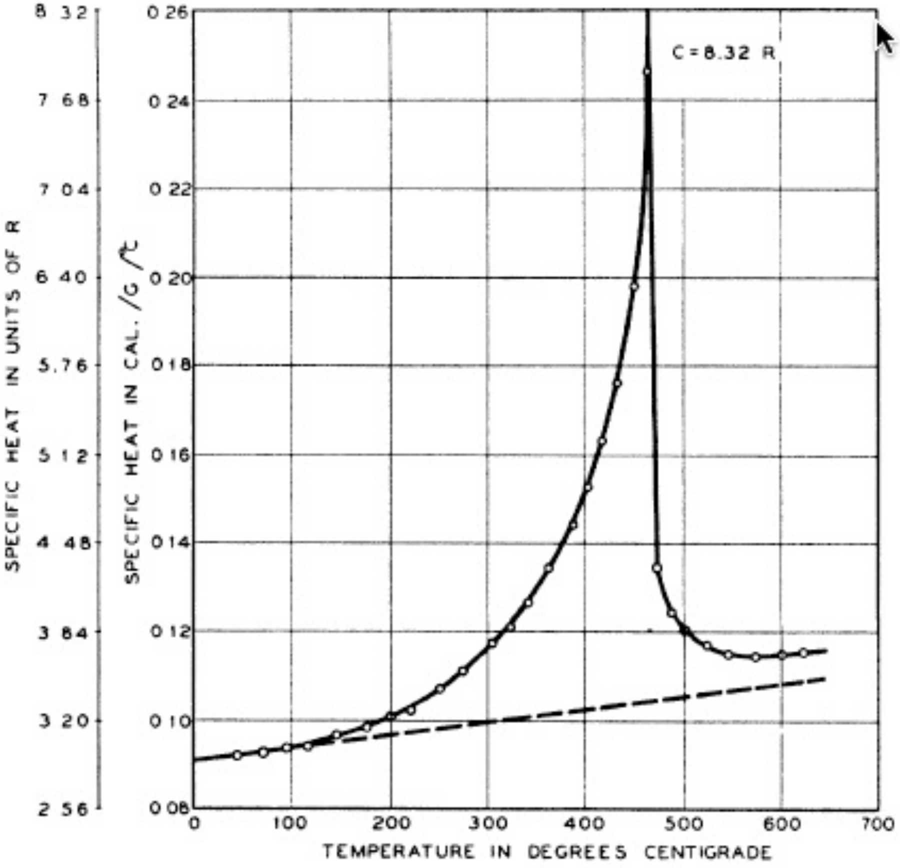


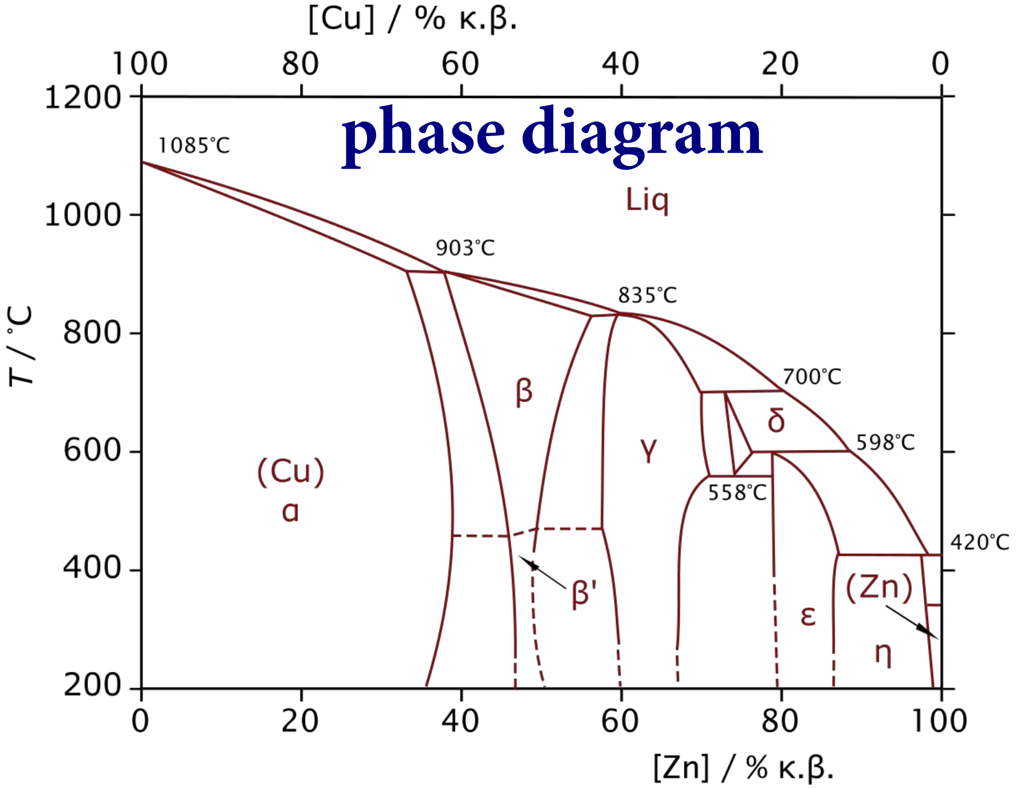
The temperature variation of the specific heat of a solid may become distinctly different from the $C_V(T)$ shown above, for example, when:

- The crystal structure changes with temperature (structural phase transition),
- An order-disorder transformation occurs,
- Additional degrees of freedom, not yet accounted for, set in.
- Any phase transition occurs.

Example: specific heat vs. temperature of a β-brass alloy, containing 48.9 at.% Zn. The dashed line is calculated from the specific heats of Cu and Zn, assuming a pure mixture

The sharp maximum of specific heat indicates a phase transition





phase diagram

[from F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938)]

Specific heat in crystalline and amorphous solids. Glasses.

Until now we did not pay any attention as to whether the solid should be considered as crystalline or amorphous.

At not too low and not too high temperatures, which are well below the melting temperature, this difference is unimportant.

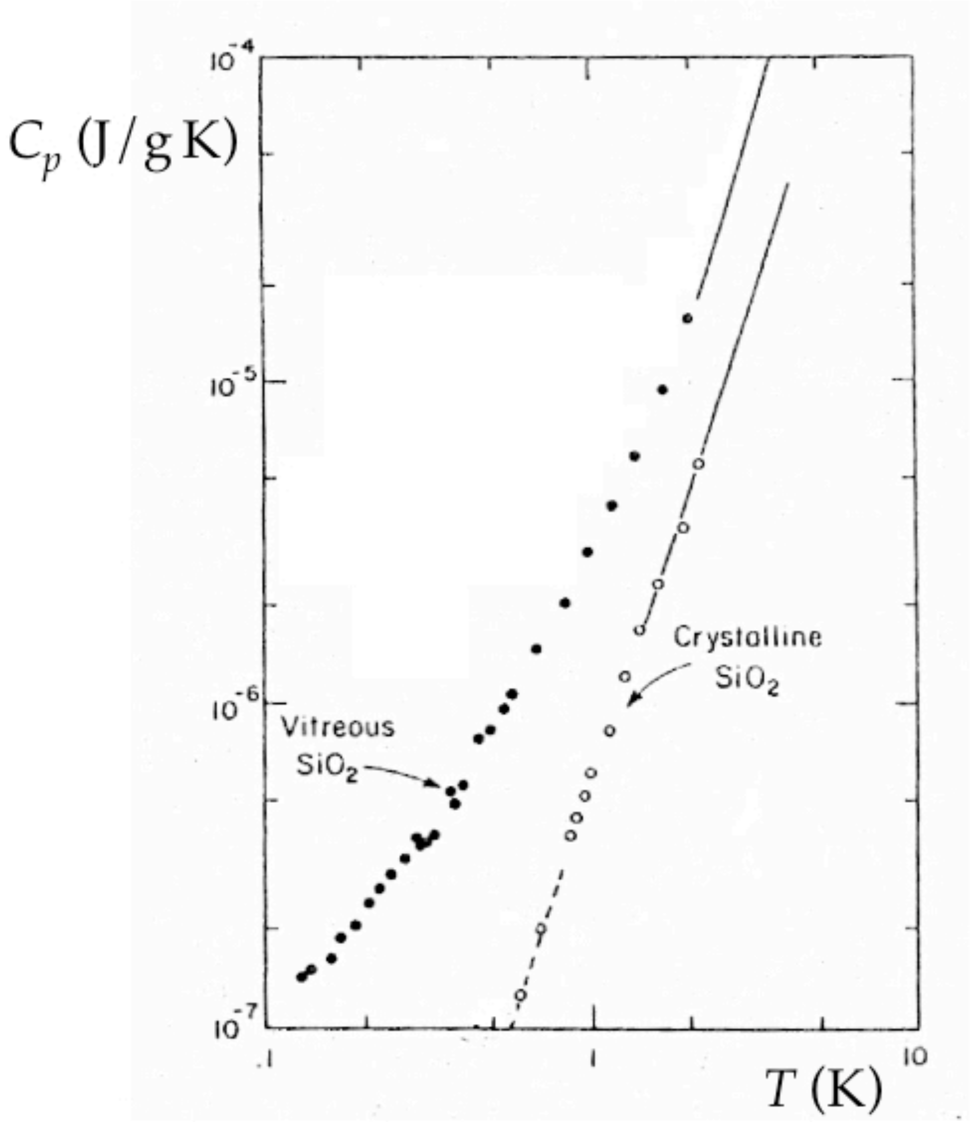
We will discuss, however, the temperature variation of the specific heat of amorphous and disordered solids that become manifest only at very low-temperatures.

Glasses and other materials with disordered structures (alloys, fractal systems) at very low temperatures display significant deviations from the specific heat vs. temperature variation described above.

This becomes apparent when the same substance is investigated both in the crystalline state and in the amorphous state.

The results of such a comparison, for the temperatures below 10 K, are shown here.

Below 1 K the specific heat of amorphous SiO_2 is several times higher than that of the crystalline SiO_2 at the same temperature.



The specific heat of glasses increases with increasing temperature as T, rather than T^3, as that of crystals.

The high specific heat of glasses was ascribed to the high degeneracy of energetically similar atomic configurations related to disorder.

Other experiments have also revealed the excess specific heat in the data obtained from crystalline alloys, although, due to lower degree of disorder than in glasses, on a smaller scale.

The specific heat anomalies of different nature have been found in systems with self-similar, or fractal, structure.