Quantum theory of the harmonic crystal

- Phonons
- Lattice specific heat
- The Einstein and Debye models
- Vibrational density of states, van Hove singularities
- Quasi-localized vibrational modes
- Localized vibrational modes
- Examples of the Einstein solids

Specific heat (definition)

and its relation to the temperature derivative of total internal energy

Change of the heat Q consists of the change of total energy + the work done:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}E}{\mathrm{d}t} + P\frac{\mathrm{d}V}{\mathrm{d}t}\ , \quad \frac{\mathrm{d}E}{\mathrm{d}t} = T\frac{\mathrm{d}S}{\mathrm{d}t} - P\frac{\mathrm{d}V}{\mathrm{d}t}\ , \quad \mathrm{d}Q/\mathrm{d}t = T\,\mathrm{d}S/\mathrm{d}t.$$

Hence, the specific heat **C=dQ/dT** is

$$C_v = T(\partial S/\partial T)_V,$$
$$C_p = T(\partial S/\partial T)_P.$$

The energy differential $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V \;\Longrightarrow\; C_v = (\partial E/\partial T)_V$

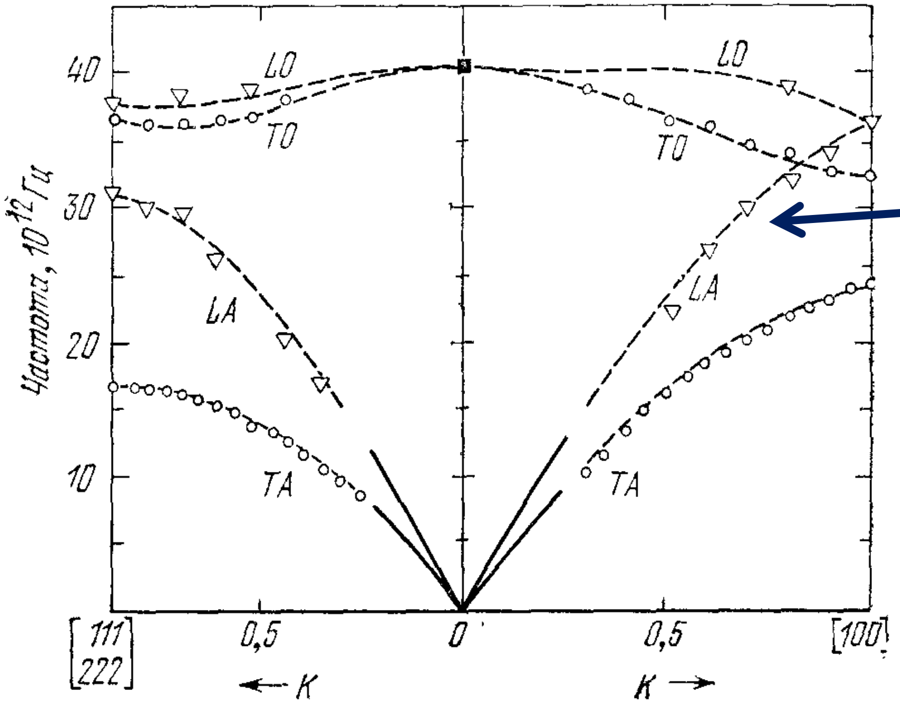
Phonon contribution to the total energy

The energy of all excitations (phonons) is given by the sum over all quantum states, which are numbered by the wave vector $\mathbf{k}=p/\hbar$:

$$E_{ph}(T)=\sum_{k,\alpha}\varepsilon_{\alpha}(k)n_{k}(\varepsilon)=\sum_{\alpha}\int\frac{Vd^{3}k}{(2\pi)^{3}}\varepsilon_{\alpha}(k)n_{k}(\varepsilon_{\alpha})$$

The filling number n_k of the quantum states of phonons is given by Bose-Einstein distribution function:

$$n_{k}(\varepsilon)=\frac{1}{\exp([\varepsilon(k)-\mu]/k_{B}T)-1}$$



The phonon dispersion $\omega(\mathbf{k})$ may consist of several branches α.

The phase volume $\int Vd^{3}k/(2\pi)^{3}$ gives the number of quantum states.

Specific heat (heat capacity of unit mass**)** $C_v = (\partial E/\partial T)_V$

Phonons

In a periodic lattice the total wave vector of interacting waves is conserved, with the possible addition of a reciprocal lattice vector $\mathbf{G}$.

Inelastic scattering: the incident particle has interacted with the lattice to destroy or create a phonon, of wave vector $\mathbf{q}$ and energy $\hbar\omega_{\mathbf{q}}$.

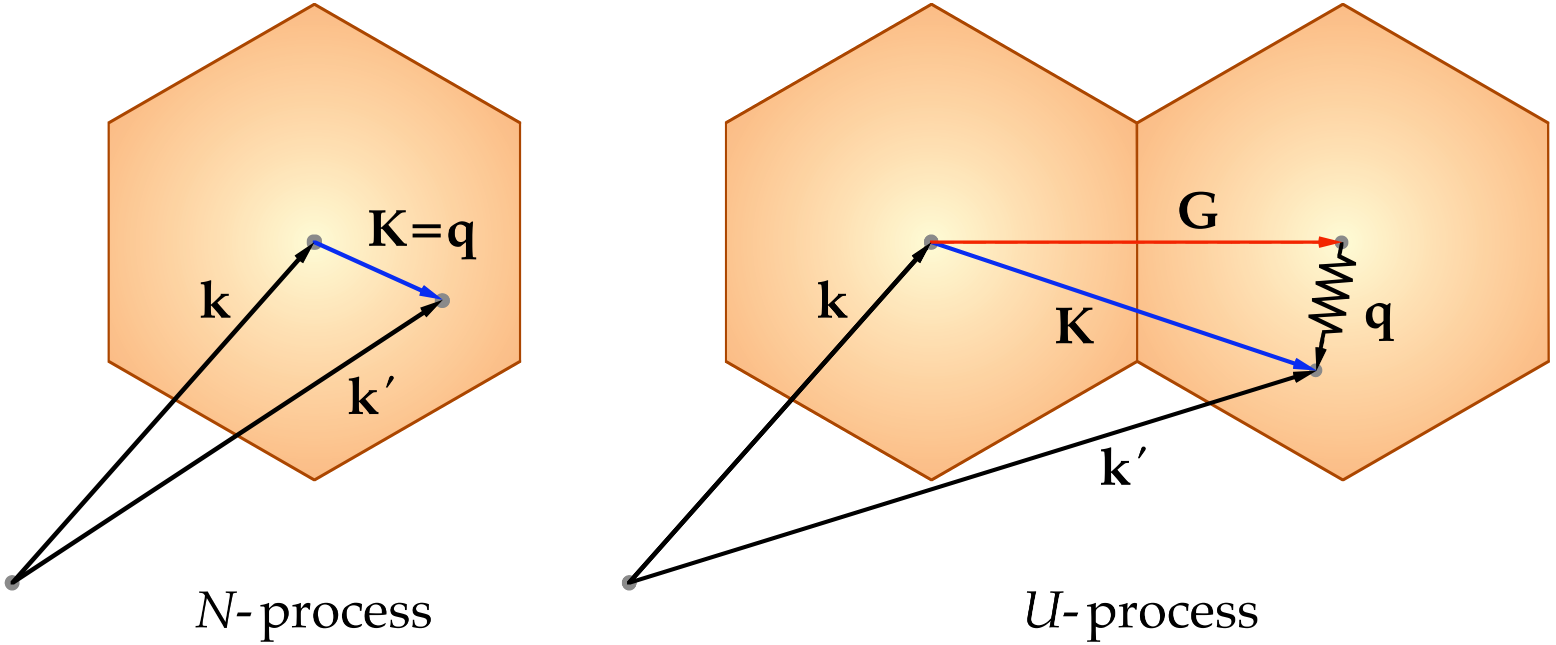
For all $\mathbf{k}'-\mathbf{k}$ values in the first Brillouin zone

$$\hbar\mathbf{k}' = \hbar\mathbf{k} \pm \hbar\mathbf{q},$$

which looks like a law of conservation of momentum.

Phonon – a quantized acoustic excitation with 'particle-like' properties, by analogy with 'photon'.

In general, the rule of conservation of momentum does not hold. The incident particle can lose, or gain, the momentum $\hbar\mathbf{G}$ in addition to the momentum of the phonon. The extra momentum $\hbar\mathbf{G}$ is transferred to the crystal as a whole. Such a process is known as an Umklapp process.



N-process

U-process

The Umklapp process is a consequence of the interplay between two scattering processes.

In one of these processes, e.g., in multi-phonon scattering, the momentum of lattice excitations, often called crystal momentum, is conserved.

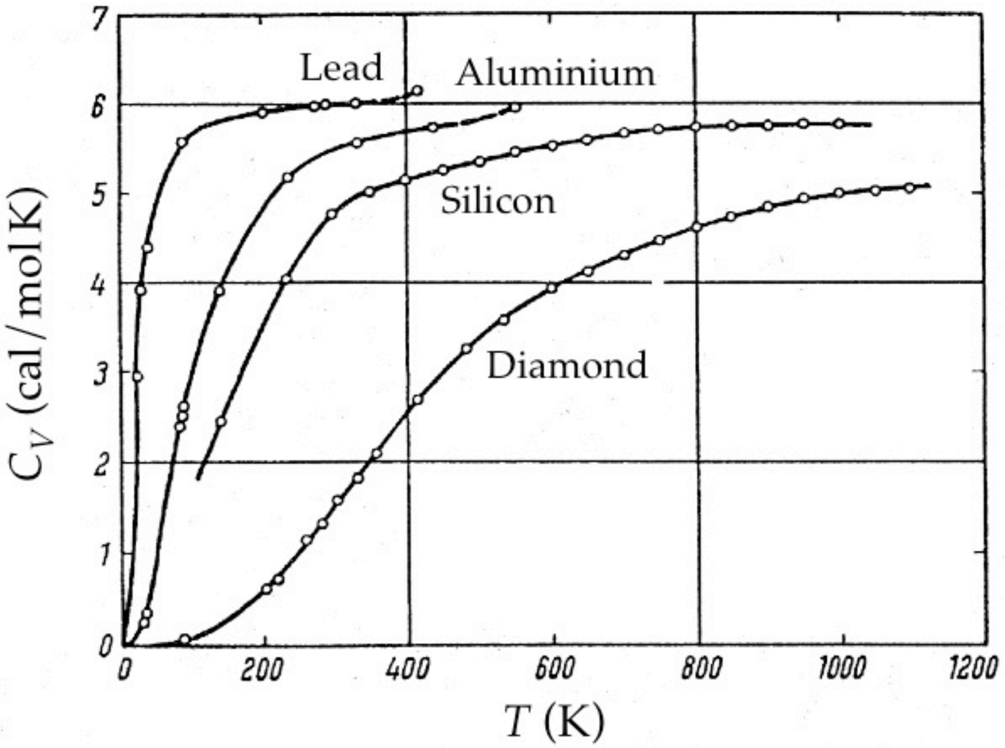
The other process, i.e., a Bragg reflection, violates the law of conservation of crystal momentum.

The characteristic time of energy transfer to the reflected acoustical wave in this process may be estimated as $\hbar / E_g$, where E_g is the energy gap in the vibrational excitation spectrum.

Often E_g is of the order of $\hbar\omega_{\max}$, where $\omega_{\max}$ is the maximum lattice frequency, and the Bragg reflection occurs very fast.

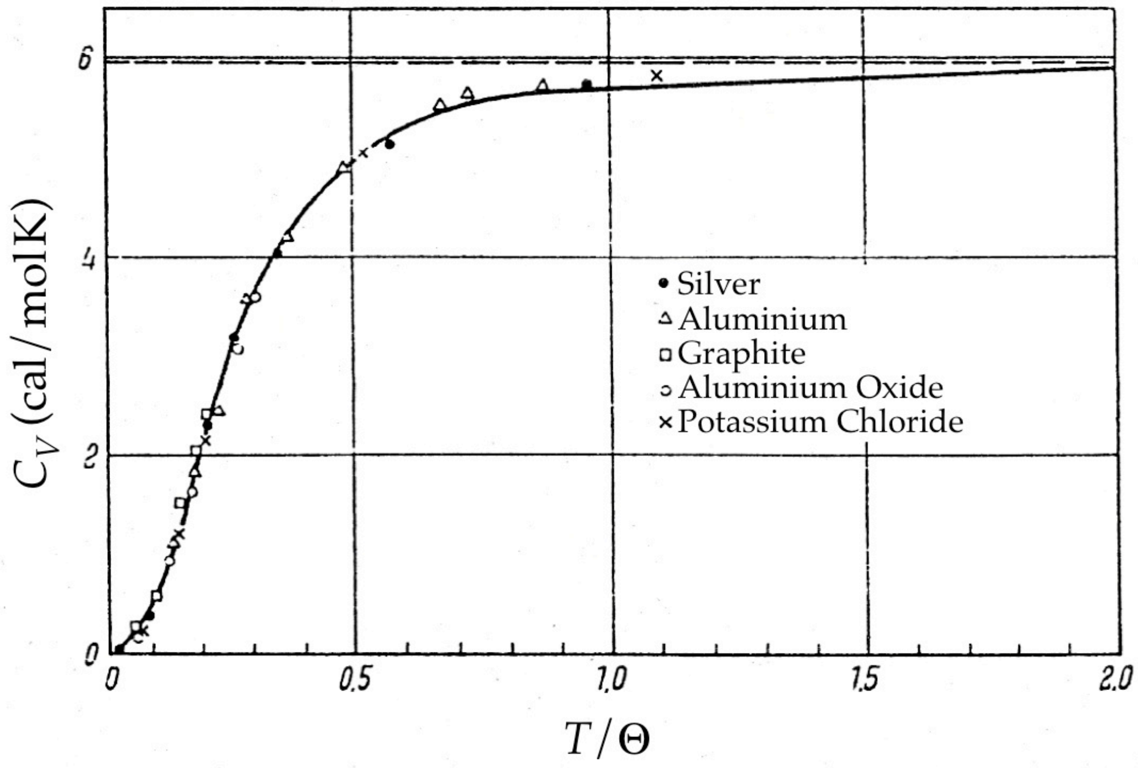
Nevertheless, the important point is that neither of the two scattering processes, if considered separately, will give rise to the same physical consequences as the Umklapp process does, i.e., finite thermal conductivity, etc.

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)]

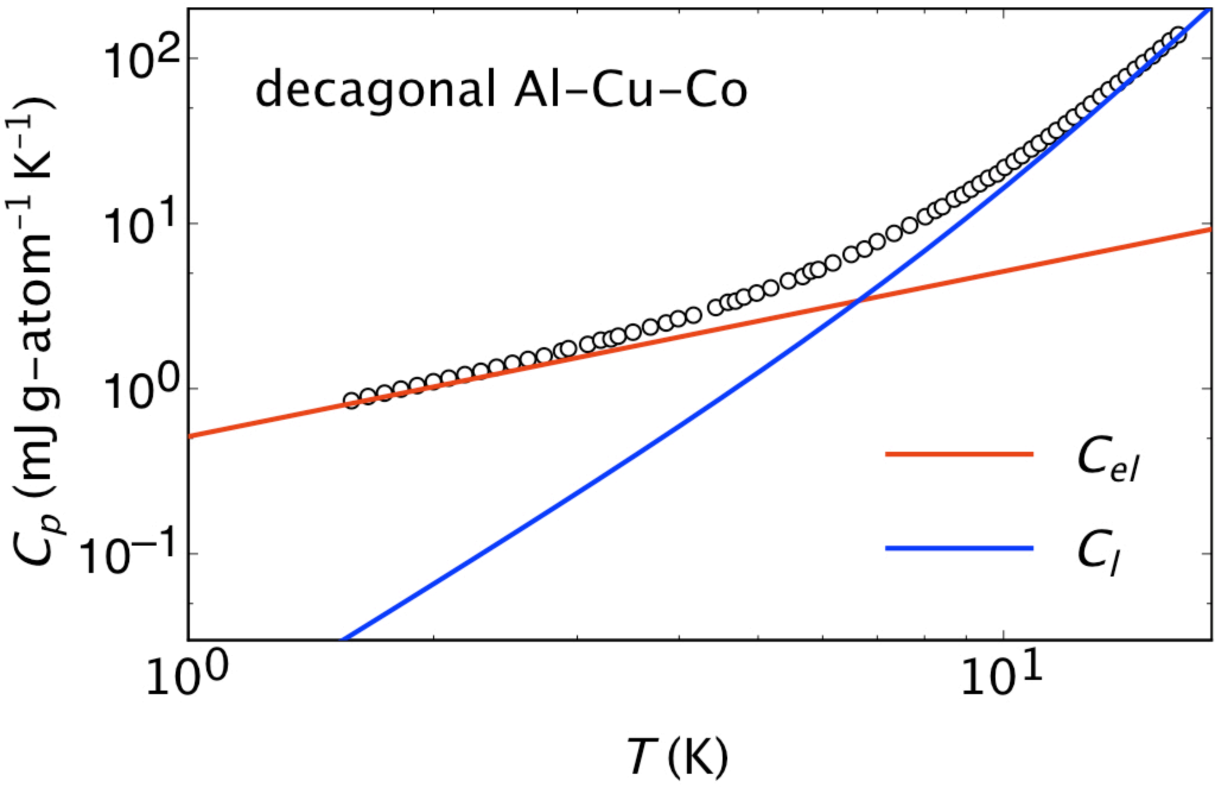
The characteristic temperature Θ plays an important role, which we will discuss later.

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.

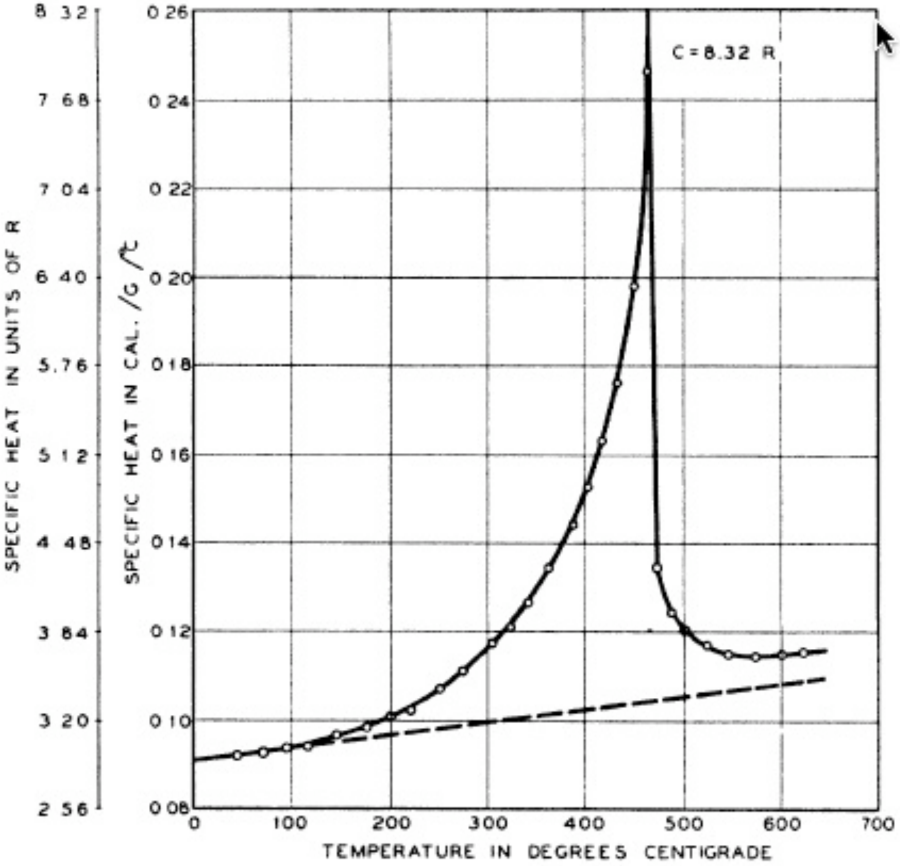


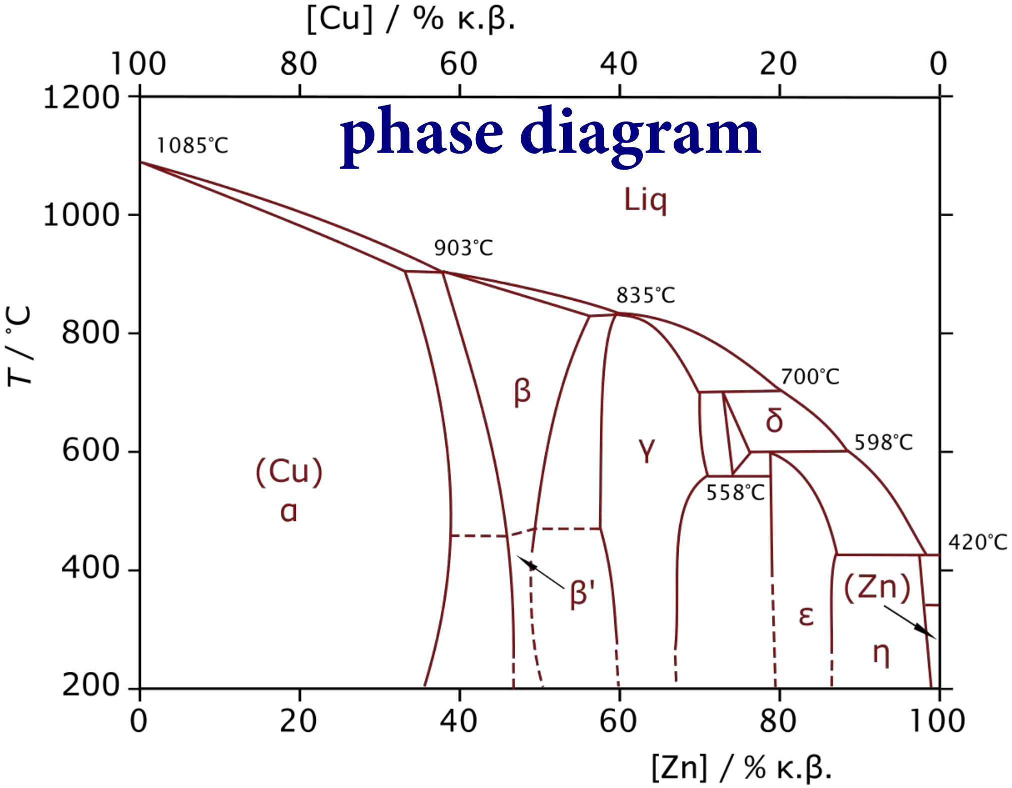
The temperature variation of the specific heat of a solid may become distinctly different from the $C_V(T)$ shown above, for example, when:

- 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.

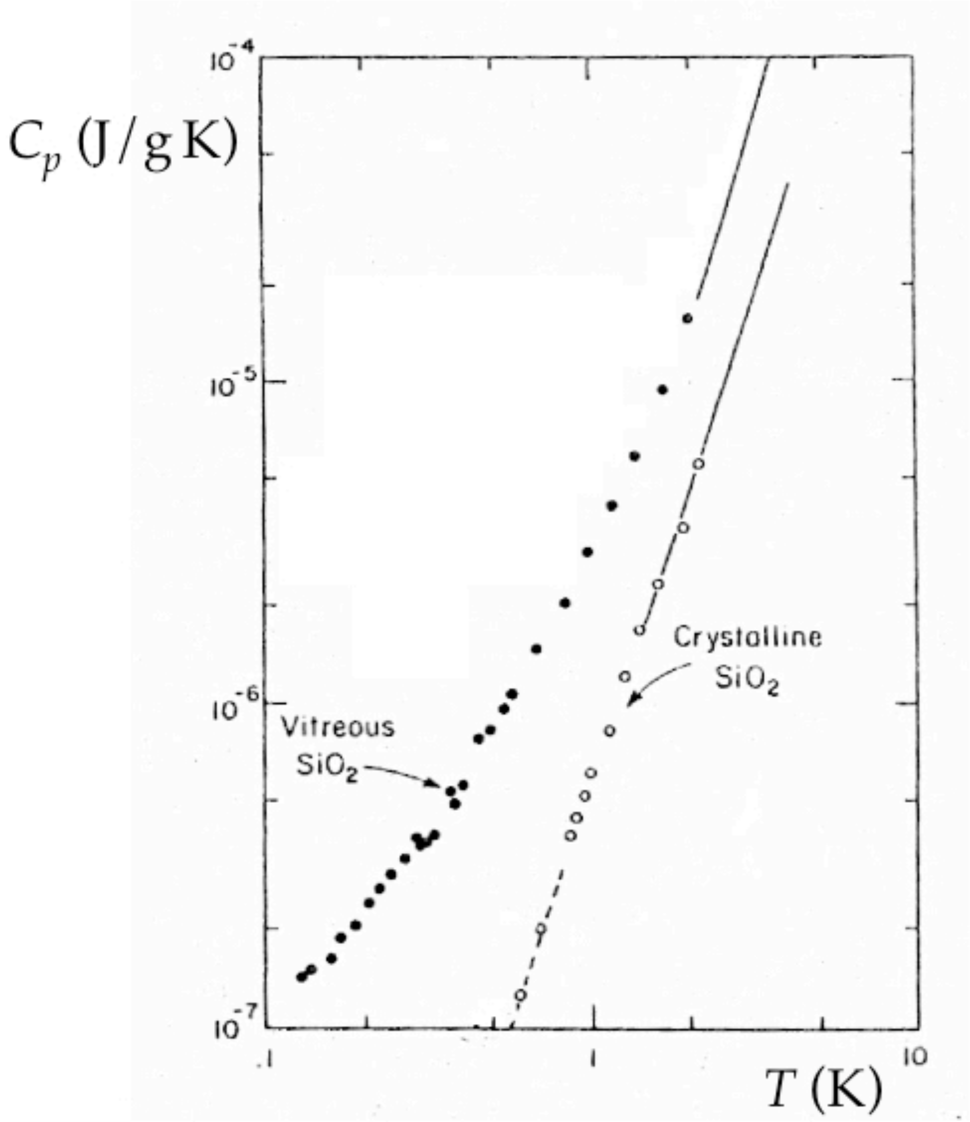
We will discuss, however, the temperature variation of the specific heat of amorphous and disordered solids that become manifest only at very low-temperatures.

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.

The Einstein model and specific heat

Classical physics cannot explain the universal C_V vs. T/Θ curve characteristic of the specific heat of solids.

Consider a solid consisting of N atoms as a system with $3N$ (more precisely $3N-6$) degrees of freedom.

Then, in the limit of high temperatures, we can approximately determine the specific heat C_V using the equipartition theorem that relates the temperature of a classical system with its average energy.

Since $U = 3Nk_BT$, we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B \ .$$

That corresponds to about 25 J/mol·K or 6 cal/mol·K and agrees well with the data.

It has been experimentally established, however, that a deviation from the Dulong and Petit law becomes more and more pronounced as the temperature decreases.

At room temperature (approx. 300 K) such a deviation is the most pronounced for diamond.

The specific heat data for diamond above 200 K have been known since 1900s from the experiments performed by H. F. Weber.

Nernst has conducted further experiments at even lower temperatures.

In 1906 Einstein has explained the observed specific heat behaviour of a solid assuming that atoms independently act as “Plank’s resonators.”

“Plank’s resonators” correspond to harmonic oscillators in quantum mechanics.

For simplicity assume that each harmonic oscillator has the same frequency ω_0.

The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega_0^2 x^2}{2} \ , \tag{5.1}$$

the energy levels are

$$E_n = (n+1/2)\hbar\omega_0\,, \quad n = 0, 1, 2, \dots \ . \tag{5.2}$$

The probability that the state with energy E_n is occupied is

$$w_n = \frac{e^{-E_n/k_B T}}{Z} \ , \tag{5.3}$$

where $Z = \sum_n e^{-E_n/k_B T}$ is the partition function.

Gibbs distribution

The average energy of an oscillator is

$$\langle E\rangle = \sum_n w_n E_n = \frac{\sum_n (n+1/2)\hbar\omega_0\, e^{-(n+1/2)\hbar\omega_0/k_BT}}{\sum_n e^{-(n+1/2)\hbar\omega_0/k_BT}} \quad . \qquad (5.4)$$

The sums in 5.4 are calculated using

$$\sum_n x^n = \frac{1}{1-x} \quad ,$$

where $x = \exp\left(-\hbar\omega_0/k_BT\right)$, and

$$\sum_n n x^n = x\frac{d}{dx}\sum_n x^n = \frac{x}{(1-x)^2} \quad .$$

We get for the average energy of an oscillator

$$\langle E\rangle = \frac{\hbar\omega_0}{2} + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} \ . \tag{5.5}$$

this is a Bose-Einstein distribution function

Here the first term on the right-hand side is the zero-point energy.

The energy of the solid is

$$U = 3N\langle E\rangle \ , \tag{5.6}$$

because each of N oscillators has 3 degrees of freedom.

The specific heat C_V of a system of N oscillators is

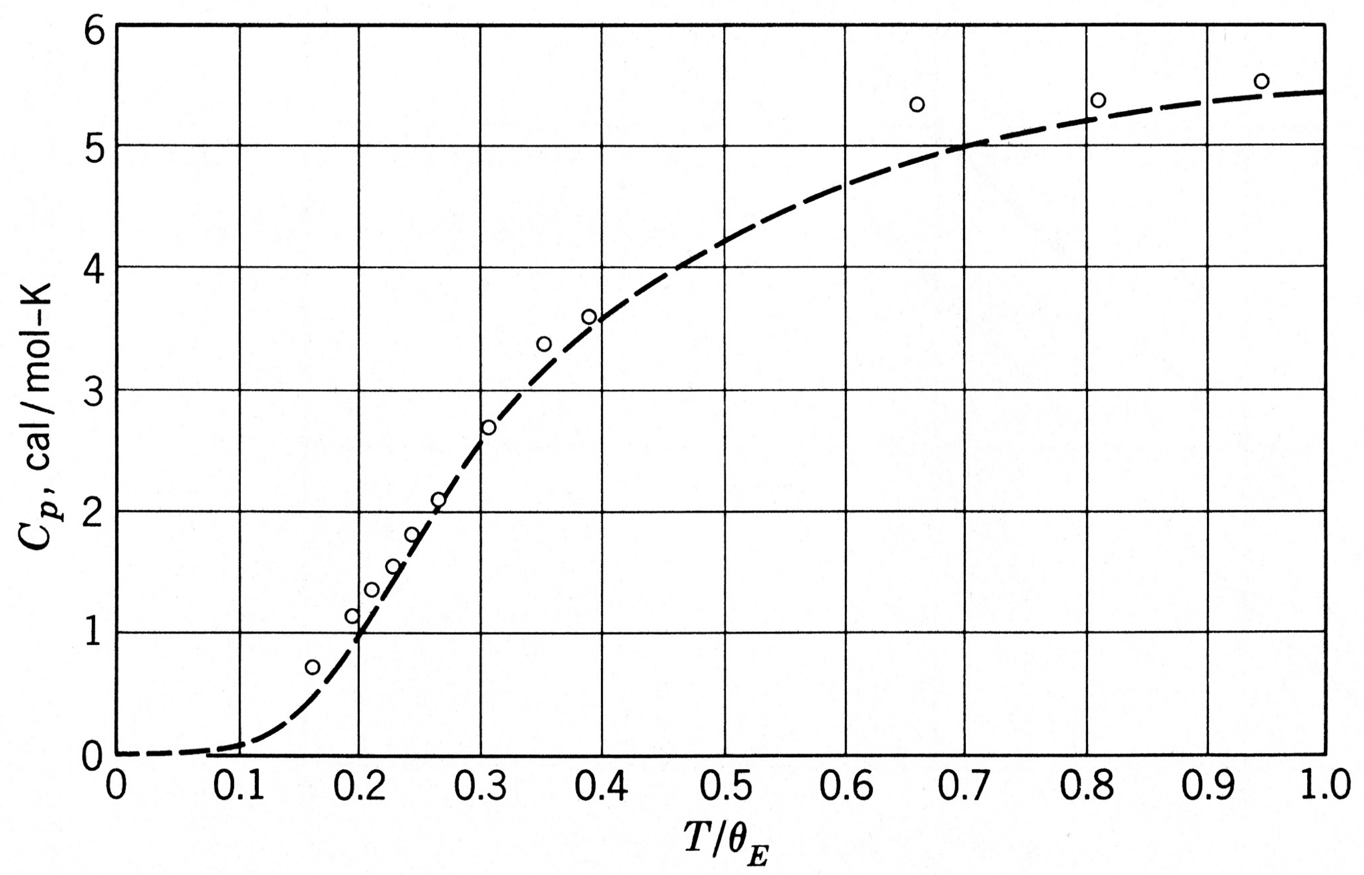
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B\left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{e^{\hbar\omega_0/k_B T}}{\left(e^{\hbar\omega_0/k_B T}-1\right)^2} \quad . \tag{5. 7}$$

The only free parameter here is the oscillator frequency ω_0, which corresponds to the Einstein temperature $\Theta_E = \hbar\omega_0/k_B$.

The temperature enters expression 5.7 as the ratio T/Θ_E.

Fitting the experimental specific heat data $C_V(T)$ using expression 5.7 yields the Θ_E value.

This figure displays the specific heat curve for diamond, calculated for $\Theta_E = 1320\,\mathrm{K}$, and the Weber's data.



[from A. Einstein, Ann. Phys., (4) **22**, 180 (1907); reproduced from Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976)]

The high-temperature limit $T \gg \Theta_E$:

$$C_V = 3k_B N e^{\hbar\omega_0/k_BT}\left[\frac{\hbar\omega_0}{k_BT\left(e^{\hbar\omega_0/k_BT}-1\right)}\right]^2 =$$

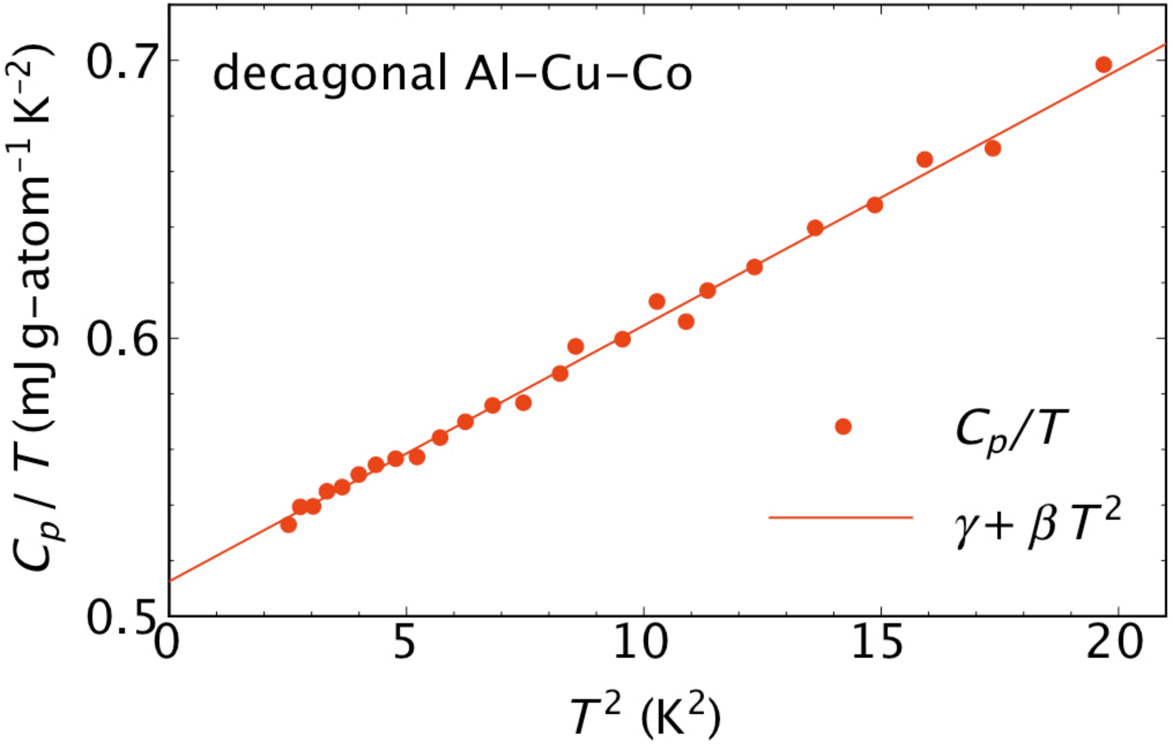
$$= 3k_B N\left(1+\frac{\hbar\omega_0}{k_BT}+\ldots\right)\left[\frac{\hbar\omega_0}{k_BT\left(\frac{\hbar\omega_0}{k_BT}+\ldots\right)}\right]^2 \approx 3k_B N\,.$$

The high-temperature specific heat of the Einstein model corresponds to the Dulong–Petit law $C_V = 3R$.

The low-temperature limit $T \ll \Theta_E$:

$$C_V = 3k_B N \left(\frac{\hbar\omega_0}{k_B T} \right)^2 e^{-\hbar\omega_0 / k_B T} \quad .$$

The lattice contribution to the low-temperature specific heat of most solids, however, varies as T^3, in disagreement with the model prediction.



The Debye model

Nernst's experiments have shown that the Einstein model does not provide a satisfactory description of the specific heat data at low temperatures.

Debye has suggested considering a solid, due to a large number of atoms, as a mechanical continuum, and thermal excitations as longitudinal and transverse elastic waves that are collective modes involving many atoms.

The Born–von Kármán periodic boundary condition.

In the Debye model we select a part of the solid in the shape of a cube with the edge L.

We seek a solution of the equation of motion representing a wave with frequency ω and wave vector $\vec{k}$

$$\vec{u}(\vec{x},t) = \vec{A}_0 e^{i(\vec{k}\vec{x}-\omega t)} \quad . \tag{5.8}$$

Here $\vec{A}_0$ is the displacement vector; for longitudinal waves $\vec{k} \parallel \vec{A}_0$ and for transverse waves $\vec{k} \perp \vec{A}_0$.

The Born–von Kármán periodic boundary condition

$$u\left(x_1, x_2, x_3, t\right) = u\left(x_1 + L, x_2, x_3, t\right) = u\left(x_1, x_2 + L, x_3, t\right) = u\left(x_1, x_2, x_3 + L, t\right) \tag{5.9}$$

leads to $k_1 = \dfrac{2\pi}{L} n_1$, $k_2 = \dfrac{2\pi}{L} n_2$ and $k_3 = \dfrac{2\pi}{L} n_3$,

where n_1, n_2 and n_3 are integers.

Each set of ***quantum*** numbers n_1, n_2, n_3 corresponds to one wave vector

$$\left|\vec{k}\right| = \frac{\omega}{c} = \frac{2\pi}{L}\left(n_1^2 + n_2^2 + n_3^2\right)^{1/2} , \qquad (5.10)$$

where c is the wave velocity.

For longitudinal waves $c = c_L$, and for transverse $c = c_T$.

The velocities of longitudinal and transverse elastic waves are given by

$$c_L^2 = \frac{E}{\rho} \text{ and } c_T^2 = \frac{G}{\rho} ,$$

respectively, where E is the Young modulus, G is the shear modulus and ρ is the density.

We will now consider waves determined by Eq. 5.8
as the normal vibrational modes of the whole solid. $\vec{u}(\vec{x},t)=\vec{A}_0 e^{i(\vec{k}\vec{x}-\omega t)}$

Contrary to the Einstein model we now allow many frequencies.

To calculate the energy of such a mechanical system we have determine the number of frequencies that fall into the range between ω and $\omega + d\omega$.

Using 5.10 we find

$$\omega = \frac{2\pi c}{L}\left(n_1^2 + n_2^2 + n_3^2\right)^{1/2} = \frac{2\pi c}{L} n \quad . \tag{5.11}$$

We can view frequencies as the points, located inside the sphere of radius $r = n$, where each point corresponds to three vibrational modes—one longitudinal and two transverse.

We have assumed that for each frequency the velocities of longitudinal and transverse waves are equal.

In the continuum approximation, the volume of the above-mentioned sphere determines the number of frequencies

$$N_\omega = \frac{4\pi}{3}\left(\frac{\omega L}{2\pi c}\right)^3 = \frac{1}{6\pi^2}\frac{\omega^3 L^3}{c^3} \quad . \qquad (5.12)$$

Correspondingly, the number of vibrational modes is

$$N_\omega = \frac{1}{6\pi^2}\omega^3 L^3 \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) \; . \qquad (5.13)$$

We define the average mode velocity $\bar{c}$ as

$$\left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) = \frac{3}{\bar{c}^3} \; . \qquad (5.14)$$

To determine the number of vibrational modes in the range between ω and $\omega + d\omega$ we can write

$$\frac{\partial N_\omega}{\partial \omega} d\omega = \frac{3}{2\pi^2} \frac{\omega^2 L^3}{\bar{c}^3} d\omega \; . \qquad (5.15)$$

The density of vibrational modes is

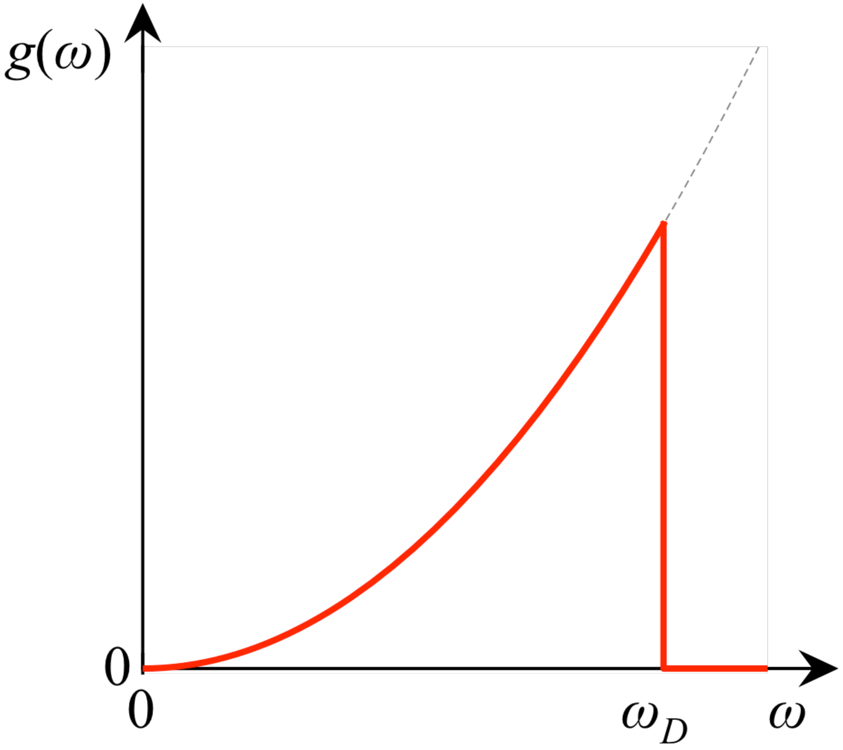
$$g(\omega)=\frac{3}{2\pi^2}\frac{\omega^2 L^3}{\bar{c}^3} \quad . \tag{5.16}$$

For an infinitely large solid the range of possible frequencies of vibrational modes would be open at the upper end.

Since we consider only a part of the solid that contains a total of N atoms, the number of possible frequencies is $3N$.

Therefore $3N=\int_0^{\omega_D} g(\omega)\,d\omega$, where ω_D is the cut-off frequency for the density of vibrational modes.

The density of vibrational modes:



Using 5.16 we find the cut-off frequency

$$\omega_D^3 = \frac{6\pi^2 N \bar{c}^3}{L^3} \quad . \qquad (5.17)$$

We now express the density of vibrational modes as a function of ω_D

$$g(\omega) = \frac{9N}{\omega_D^3}\omega^2 \ . \tag{5.18}$$

We now again assume that every vibrational mode corresponds to a harmonic oscillator, whose average energy $\langle E \rangle$ is given by Eq. 5.5.

Then the total energy of the part of the body containing a total of N atoms is

$$U = \int_0^{\omega_D} g(\omega)\langle E \rangle d\omega \ . \tag{5.19}$$

Combining Eqs. 5.5, 5.18 and 5.19 we find

$$U = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \omega^2 \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} d\omega \ . \qquad (5.20)$$

Here we account only for the temperature dependent contribution to $\langle E \rangle$ and do not consider the zero-point energy.

The cut-off frequency ω_D corresponds to the so-called Debye temperature

$$\Theta_D = \frac{\hbar\omega_D}{k_B} \ . \qquad (5.21)$$

Changing the integration variable in Eq. 5.20 to $x = \hbar\omega / k_B T$ yields

$$U = 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x}{e^x - 1} dx \ . \tag{5.22}$$

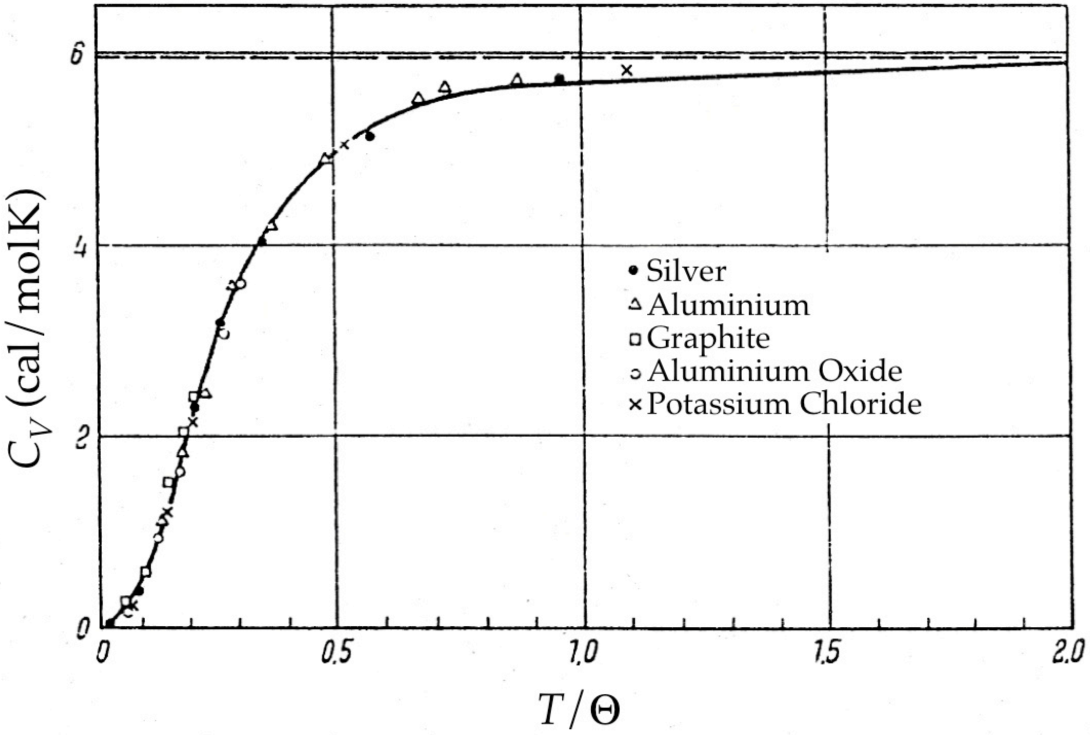
Here the upper limit of integration is $x_D = \hbar\omega_D / k_B T = \Theta_D / T$.

Differentiating with respect to T we get the specific heat

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \ . \tag{5.23}$$

As in the Einstein model, the specific heat depends only on the dimensionless variable T/Θ_D.

Here the curve corresponds to the Θ_D values, obtained by fitting the specific heat data using Eq. 5.23; the Θ_D values are, of course, material-dependent.



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

The high-temperature limit $T \gg \Theta_D$:

$$U(T) = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3 \left.\frac{x^3}{3}\right|_0^{\frac{\Theta_D}{T}} = 3Nk_BT \ .$$

The high-temperature specific heat corresponds to the Dulong–Petit law $C_V = 3R$.

The low-temperature limit $T \ll \Theta_D$:

$$U(T) = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3 \underbrace{\int_0^\infty \frac{x^4 e^x}{(e^x-1)^2}\,dx}_{\frac{4\pi^4}{15}} \ .$$

This definite integral can be evaluated exactly.

The low-temperature specific heat is

$$C_V = \frac{12}{5}\pi^4 N k_B \left(\frac{T}{\Theta_D}\right)^3 \ .$$

The Debye approximation correctly describes the lattice contribution to the specific heat at low temperatures $T < \frac{1}{20}\Theta_D$.

Assuming that the parameters c_l and c_t are the velocities of the compressional and shear sound waves, we can calculate the cut-off frequency ω_D and, consequently, Θ_D using Eqs. 5.14 и 5.17.

Debye model for crystals

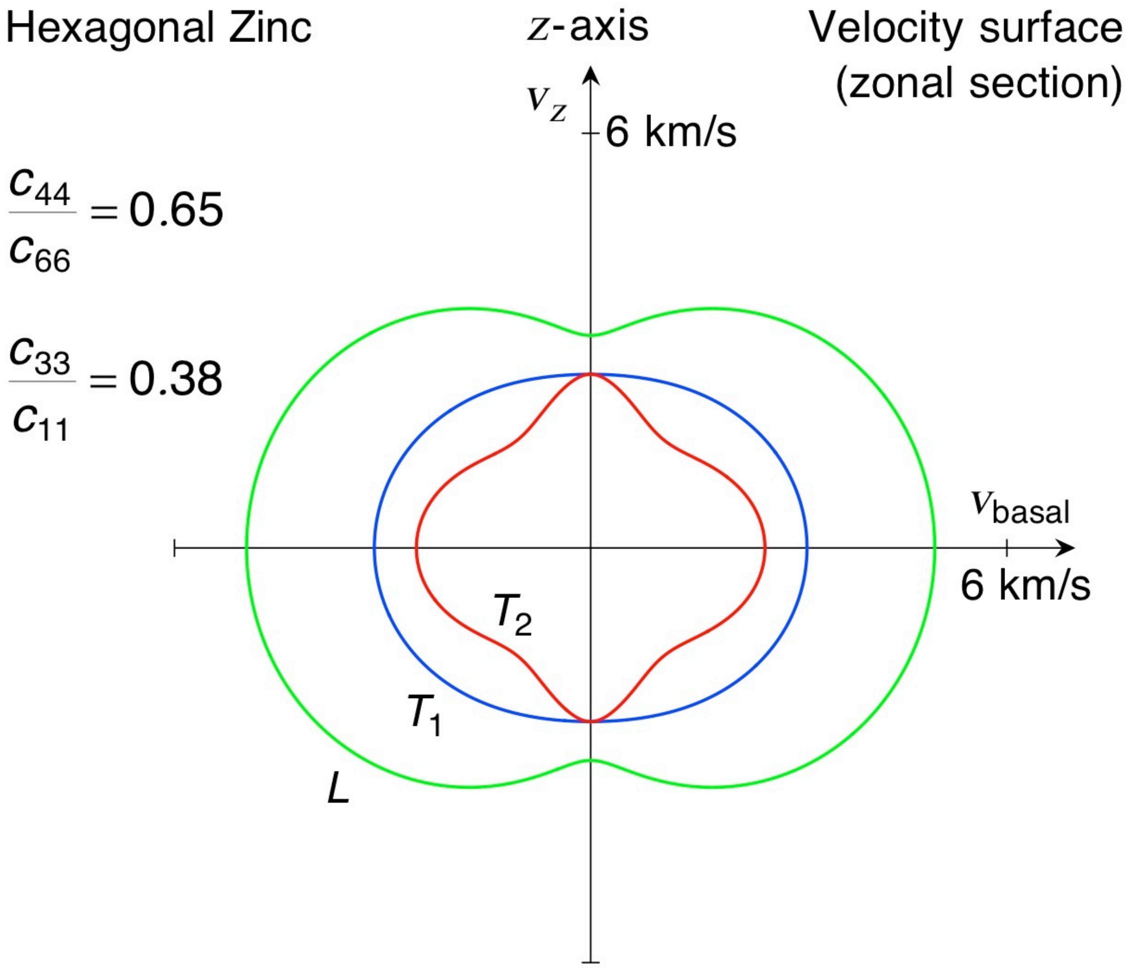
Expressing the sound velocities in terms of the elastic constants allows us to generalize the Debye approximation to include anisotropic media. Consider hexagonal crystals, which have five independent elastic constants and are transversely isotropic. The sound velocities are given by

$$\rho v_{T_1}^2 = c_{44} + \frac{1}{2} c \sin^2 \theta$$

$$\rho v_{L,T_2}^2 = c_{44} + \frac{1}{2} \Big\{ a \sin^2 \theta + h \cos^2 \theta \pm \left[(a \sin^2 \theta + h \cos^2 \theta)^2 - 4(ah - d^2) \sin^2 \theta \cos^2 \theta \right]^{\frac{1}{2}} \Big\},$$

where $a = c_{11} - c_{44}$, $c = c_{11} - c_{12} - 2c_{44}$, $d = c_{13} + c_{44}$, $h = c_{33} - c_{44}$.

As an example, we show the $v_i(\theta)$ variations for Zinc.



At low temperatures only the long-wavelength acoustic modes contribute to $C_V(T)$, which takes the form

$$C_V(T) = \frac{2\pi^2 k_B^4}{5\hbar^3 \overline{v}^3} T^3 \quad .$$

Here $1/\overline{v}^3$ is the average of the inverse third power of the velocities of the three acoustic modes:

$$\frac{1}{\overline{v}^3} = \frac{1}{3}\sum_{i=1}^{3}\int_0^{\pi} \frac{1}{v_i^3(\theta)} \frac{\sin\theta d\theta}{2} \quad .$$

The Debye temperature is given by

$$\Theta_D = \frac{\hbar}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3} \overline{v} \quad ,$$

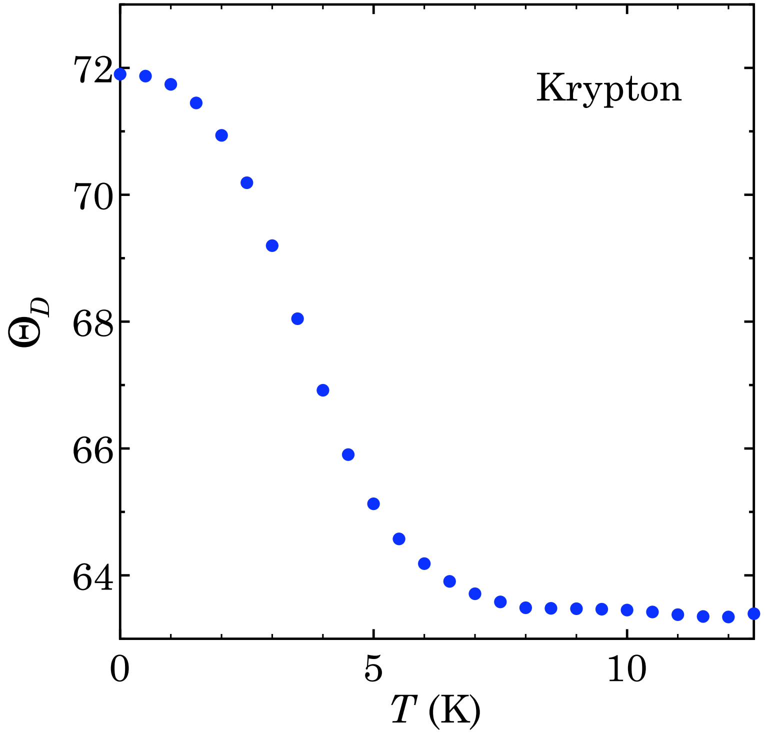
where N/V is the number density of atoms.

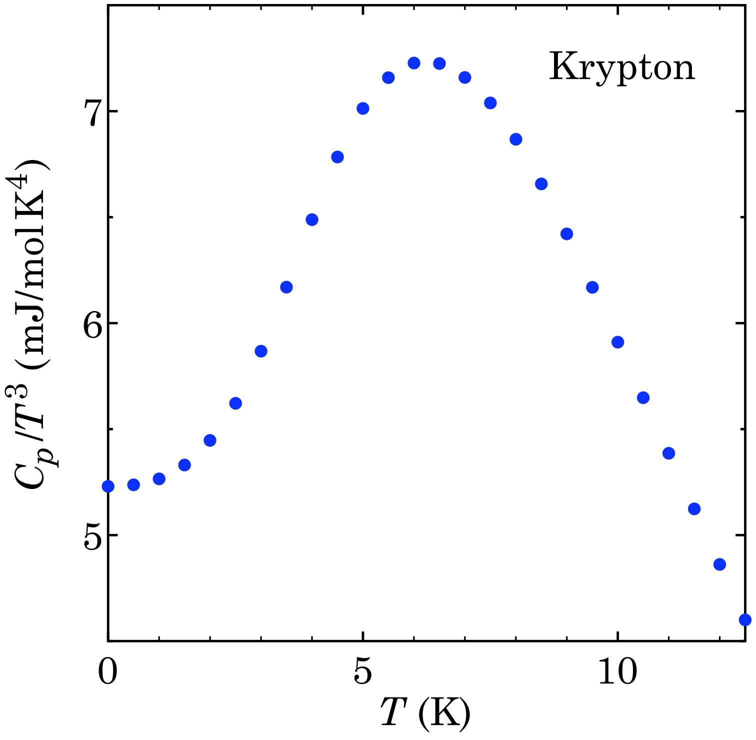
Here we compare for several solids the Debye temperatures Θ_D, obtained from fitting the measured specific heat data $C_p(T)$ at low temperatures and calculated from elastic constants c_{ij}.

	C (diamond)	Si	V	Fe	Cu	Al	Pb
Θ_D (K) from $C_p(T)$	2240	647	326	457	342	423	102
Θ_D (K) from c_{ij}	2240	649	399	477	345	428	105

[from K. A. Gschneider, Jr., in *Solid State Physics*, vol. 16, eds. F. Seitz and D. Turnbull (Academic Press, New York, 1964) p. 275]

Sometimes the $C_p(T)$ data in the intermediate temperature range is analyzed assuming that Θ_D explicitly depends on temperature.





[Data from L. Finegold and N. E. Phillips Phys. Rev. **177**, 1383–1391 (1969)]

The Debye model is quite successful in describing the temperature variation of the specific heat of insulators.

We remind, however, that the Debye model treats a solid as a continuum, i.e., disregards atomic structure of a crystal lattice, and assumes no dispersion in the excitation spectrum of the vibrational modes.

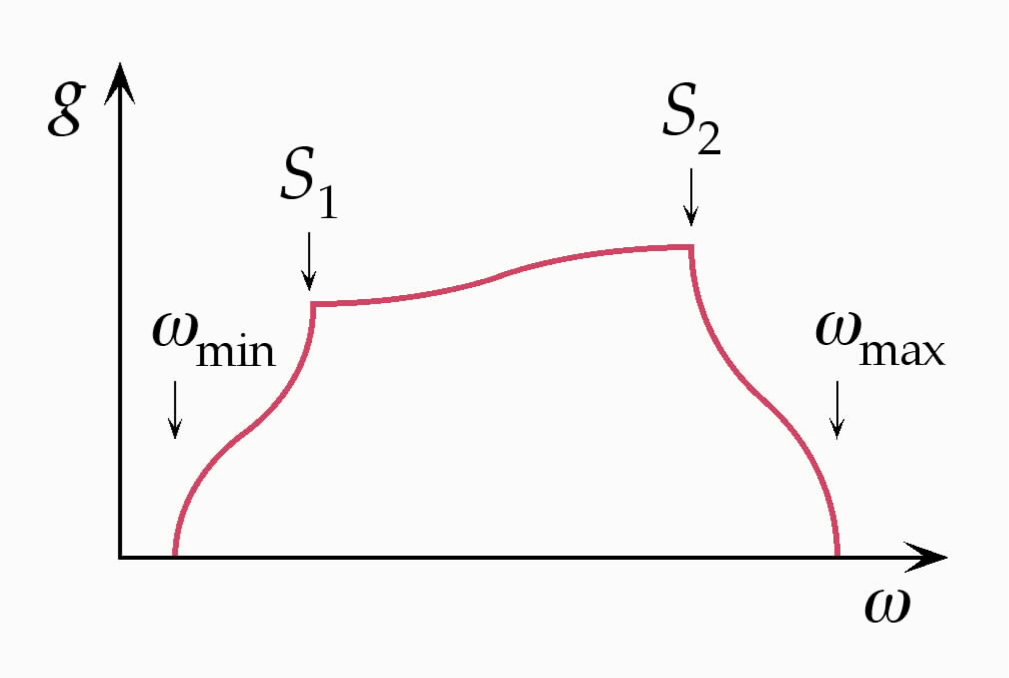
Density of normal modes, van Hove singularities

In three dimensions the density of normal modes $g(\omega)$ becomes quite complex because ω now depends both on the absolute value and on the direction of the wave vector $\vec{k}$.

The critical points of the density of normal modes $g(\omega)$, related to vanishing of the absolute value of the group velocity $v_{\mathbf{k}}$, are known as the van Hove singularities.

Contrary to the one-dimensional case, the van Hove singularities are infinities only in the $g(\omega)$ derivatives, but not in $g(\omega)$ itself.

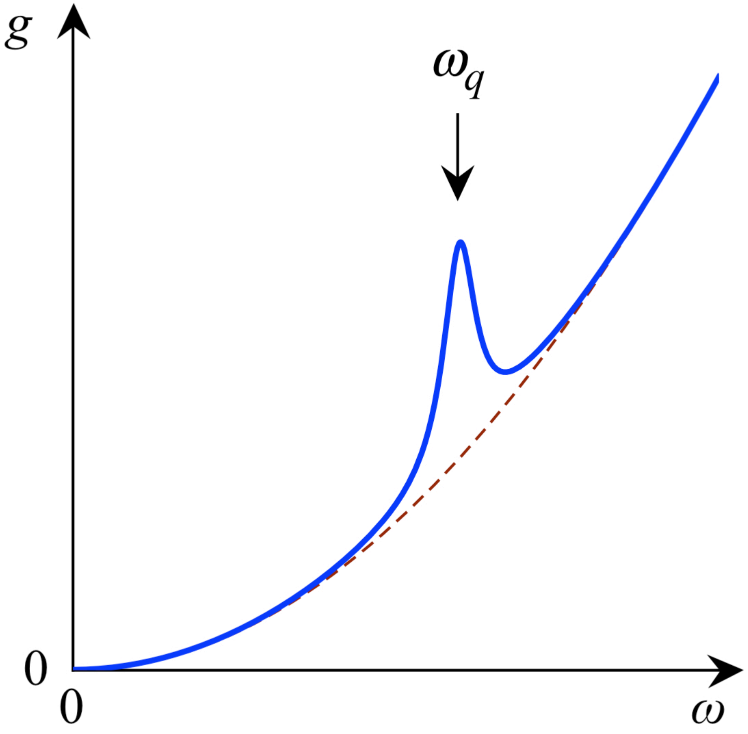
There are four types of critical points: minimum, saddle-points S_1 and S_2 and maximum.



Van Hove's theorem states that the density of normal modes $g(\omega)$ must contain at least one critical point of each of the types S_1 and S_2, and $dg/d\omega \to -\infty$ at the upper end.

Quasi-localized vibrational modes

Heavy impurities, for example, heavy isotope impurities, in a monoatomic lattice lead to a Lorentz-type feature in the density of vibrational states at $\omega_q \ll \omega_D$



$$\delta g(\omega) \sim \frac{\omega_q \Gamma_q}{\left(\omega^2 - \omega_q^2\right)^2 + \Gamma_q^2} \; .$$

Here ω_q is the quasi-local frequency and Γ_q is the half-width of the Lorentz curve.

Since

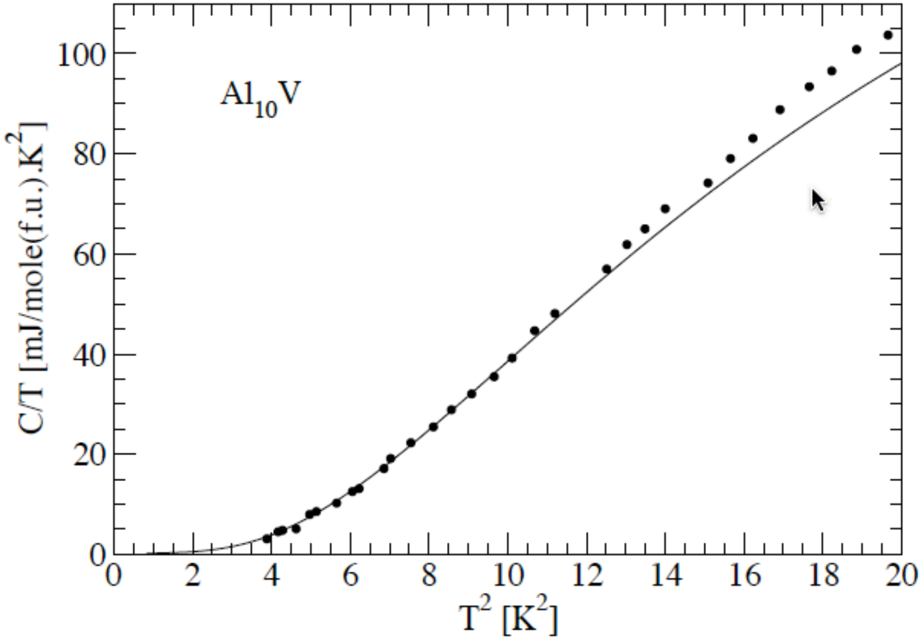
$$\frac{\Gamma_q}{\omega_q^2} \sim \frac{m' - m}{m} \ ,$$

where m and m' are the host and impurity atomic masses, respectively, the Lorentz curve narrows as $m' - m$ increases.

Quasi-local vibrations alter the thermodynamic and kinetic properties of a crystal, in particular, resulting in resonance anomalies in the absorption of ultrasound waves.

Local phonon modes; the Einstein solids

The specific heat of $Al_{10}V$ above 2 K is well described by the Einstein model, i.e., it increases exponentially with increasing temperature [A. D. Caplin *et al.*, 1973].



[from L. Bodnárová, Diploma Thesis, Comenius University, Bratislava, 2004]

This phenomenon relates to a well-defined local phonon mode that has an Einstein temperature of 22 K.

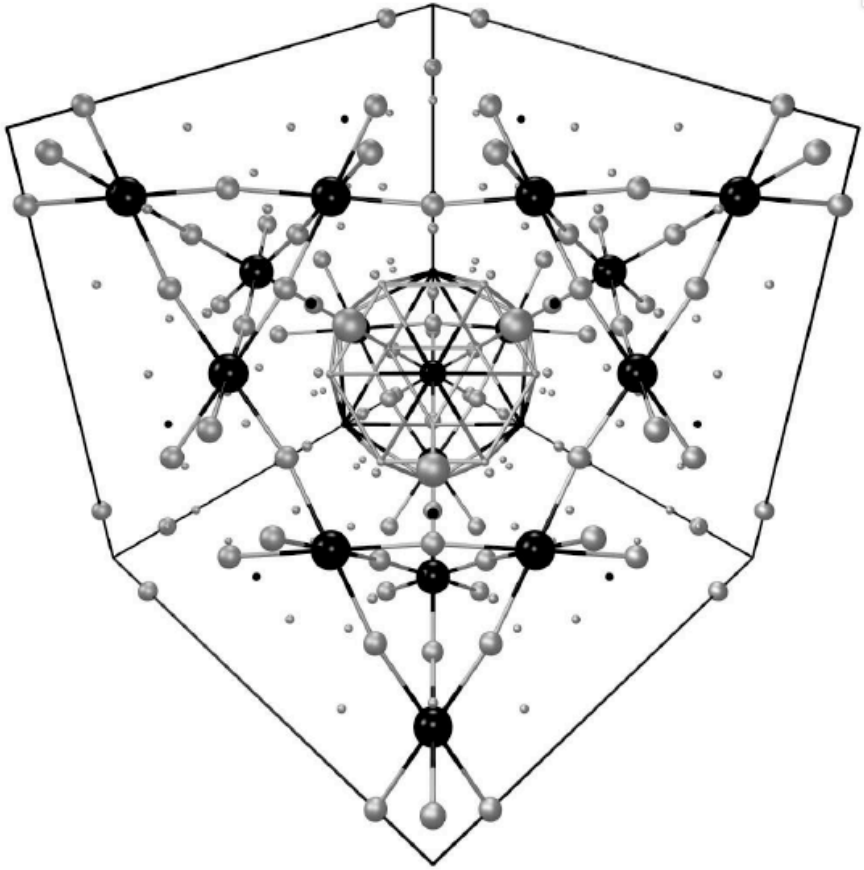
It is thought that vibrations of ‘loose’ Al atoms, occupying the centers of Friauf polyhedra in the $Al_{10}V$ structure, are responsible for the local modes.

The Friauf polyhedron is composed of 16 Al atoms. It can be viewed as a large ‘shell’ of about 3.2 Å in radius.

For comparison, the separation between nearest neighbours in the fcc structure of Al is only 2.8 Å.

Consequently, Al atoms inside the Friauf polyhedra move in a shallow potential resulting in vibrational modes with very low energies; such Al atoms are effectively uncoupled from the rest of the $Al_{10}V$ structure.

The space group of $Al_{10}V$ is $Fd\bar{3}m$. The primitive cell contains 44 atoms. The cubic unit cell consists of four primitive cells. The grey and black spheres are the Al and V atoms, respectively. There are eight 'holes' per unit cell.



[from L. Bodnárová, Diploma Thesis Comenius University, Bratislava, 2004]

Another example of an Einstein solid is quinol clathrate with an argon atom trapped inside a cage in its structure. In this case the Einstein temperature is 48 K [Parsonage and Stavely, 1960].